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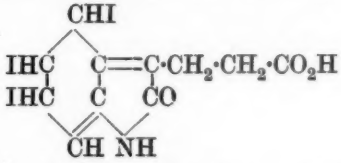
CIX.—*The Relationship of Thyroxin to Tryptophan.*

By C. STANTON HICKS.

THYROXIN, the crystalline compound obtained from the thyroid gland by hydrolysis (Kendall, *J. Biol. Chem.*, 1919, **39**, 125; **40**, 265) has not been studied by any other observer with a view to corroborate or otherwise the evidence for its highly interesting structural formula as put forward by Kendall (*ibid.*, 1919, **40**, 268).



As was appreciated at the time, and pointed out by Barger (*Ann. Reports*, 1919, **16**, 160), the presence or absence of two additional hydrogen atoms in the benzene nucleus of the molecule as figured by Kendall would make only the small difference of 0·35% in the total hydrogen content, and such a substance, containing as it does some 67% of iodine and only 1·60% of hydrogen, offers difficulties to exact analysis. The substance also contains three asymmetric carbon atoms; this was unappreciated in the original paper (*loc. cit.*, p. 308).

In connexion with work on the etiology of goitre, it was considered that, assuming Kendall's formula to be correct, or substantially so, a likely starting point for the synthesis of thyroxin in the animal body would be tryptophan. In his original paper, Hopkins had suggested that tryptophan, the metabolism of which in the organism is as yet unknown, and which is of such vital importance for the life and growth of the animal, might be used in the manufacture of some internal secretion (*J. Physiol.*, 1901–2, **27**, 418; also 1912, **44**, 425). He further was able to show that tryptophan was not synthesised in the animal body.

Two methods were adopted in the initial investigation into the relationships of thyroxin and tryptophan. Rats were placed on diets containing known deficiencies of tryptophan, with the intention of following (*a*) basal metabolism changes, and (*b*) pathological changes in the thyroid and suprarenal glands, and a study of the ultra-violet absorption spectra of the two compounds was made. The former work, which is not yet complete, will be reported elsewhere. This paper is a preliminary one only, on the absorption spectrum relationships.

Apparatus.—A Hilger spectrometer for the ultra-violet, with a

rotating sector photometer, was first calibrated against a pure cadmium emission spectrum, using the high-tension condenser electric discharge, with cadmium electrodes. Subsequent absorption measurements were made using nickel electrodes, which give a spectrum rich in lines, beyond 2100 Å.U. A Sartorius micro-balance accurate to 0·00001 g. was used in making up the solutions for measurement.

Method.—Thyroxin "crystals" were obtained from Messrs. Squibb and Son of New York, and, in all, 20 mg. of the substance were used. The thyroxin was recrystallised by slowly passing carbon dioxide into its solution in *N*-sodium hydroxide (4 equivs., calculated from the formula). Thyroxin dissolves with great difficulty, and requires a high local concentration of alkali; in no case did the substance dissolve in its equivalent of sodium hydroxide as stated by Kendall and Osterberg (*J. Biol. Chem.*, 1919, **40**, 268). This may have been due to the thyroxin (Squibb) not being pure enough, for on account of losses in dealing with small amounts of material, and the high cost of the substance, solubility experiments were not attempted on the crystals isolated in this work.

The thyroxin was separated from the solution in a centrifuge, washed by centrifuging with water, and dried in a vacuum desiccator. The melting point, determined under the microscope by comparison with that of phenolphthalein, was about 250° as nearly as could be estimated, as browning and decomposition began near this point. Under the microscope, the sheaves of needles depicted in the original paper were observed.

The absorption spectra were best obtained with aqueous alkaline solutions, prepared by suitably diluting a solution of thyroxin in alkali (4 equivs.). Using a 10 millimetre cell, and a comparison solution of alkali of equal concentration, a series of 18 photographs was taken at each of the following dilutions: *M*/8,000, *M*/12,000, *M*/16,000, *M*/20,000, *M*/30,000, *M*/40,000. The handling of such small amounts of material was the chief source of difficulty, and measurements were made in duplicate where possible.

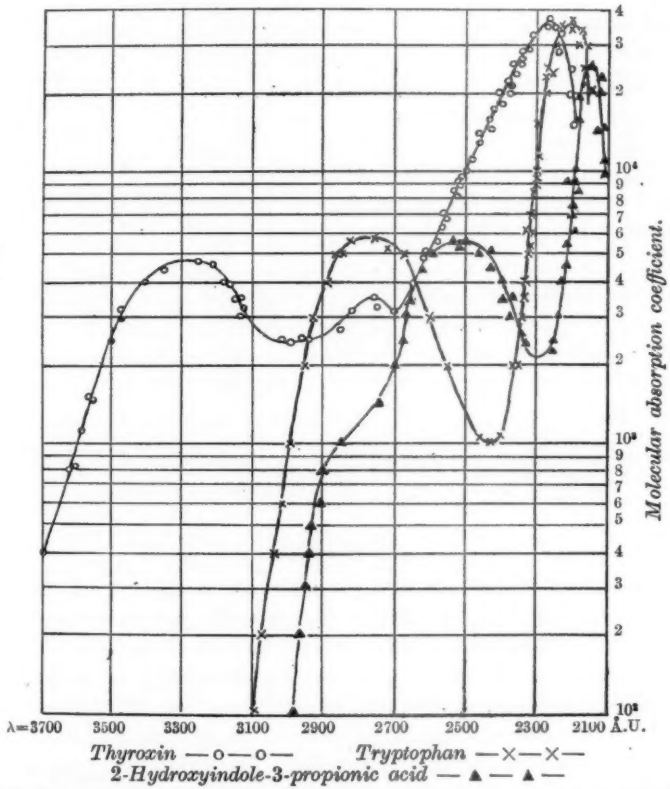
According to Kendall, the enolic form will be present in the alkaline solution (*loc. cit.*).

Tryptophan was prepared by Onslow's modification (*J. Physiol*, **29**, 451) of Hopkins and Cole's method (*ibid.*, 1901—2, **27**, 418). The product was extracted by butyl alcohol in a vacuum after Dakin (*Biochem. J.*, 1917—18, **12**, 290; *J. Biol. Chem.*, 1920—21, **44**, 499), decolorised with animal charcoal, and recrystallised from 65% alcohol; m. p. 289°.

Measurements were made in alcoholic solution at concentrations of *M*/10,000, *M*/30,000, *M*/40,000, *M*/50,000.

2-Hydroxyindole-3-propionic acid was recrystallised from water and its absorption spectra were measured in concentrations of $M/10{,}000$, $M/20{,}000$, $M/30{,}000$, $M/40{,}000$, and $M/50{,}000$.

In order to compare the effect of substitution of iodine in the molecule on the absorption curve of tryptophan with that due to the iodine in thyroxin, attempts were made to prepare iodotryptophan,


Molecular absorption coefficient.
λ=3700 3500 3300 3100 2900 2700 2500 2300 2100 Å.U.
Thyroxin —o—o— Tryptophan —×—×—
2-Hydroxyindole-3-propionic acid — ▲ — ▲ —

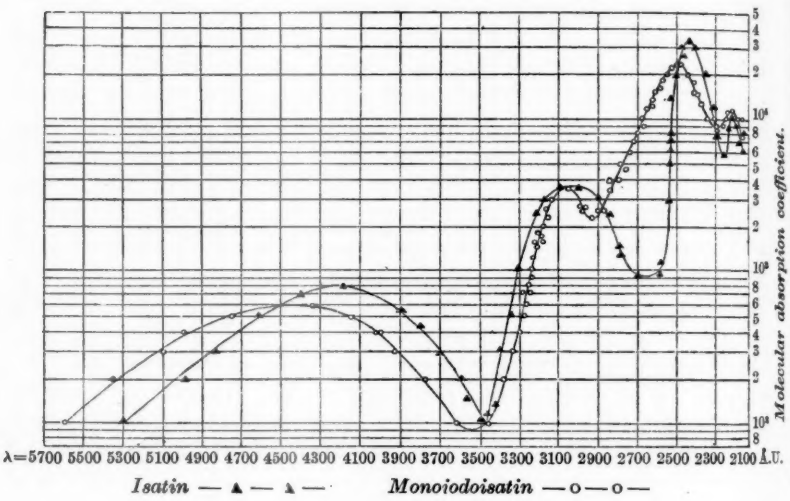
Molecular absorption coefficient $= 1/d.\ (\log I_0 - \log I)/c$; *where* I_0 *= intensity of incident light;* I *= intensity of transmitted light;* d *= thickness of absorbing layer in cm.; and* c *= molecular concentration.*

but the resulting compound has not so far been obtained with a constant composition (compare Neuberg, *Biochem. Z.*, 1907, **6**, 276, and Koch, *J. Biol. Chem.*, 1913, **14**, 106).

Monoiodoisatin was therefore prepared by treating a saturated solution of isatin (m. p. 201°) in glacial acetic acid with iodine monochloride, more than three times the theoretical amount being necessary (compare Borsche and others, *Ber.*, 1924, **57**, [*B*], 1770; Michael and Norton, *Ber.*, 1878, **11**, 107). The compound separate l

in brilliant, glistening, scarlet, crystalline powder form, m. p. 264·5—265·5°, and was very sparingly soluble in alcohol or glacial acetic acid (Found: I = 46·05, 46·31. Calc., I = 46·12%).

A large series of dilutions was used, from $M/3000$ to $M/30{,}000$ by steps of $M/3000$, in order to ensure that no small variations in the curve were overlooked.



Discussion.

Examination of the ultra-violet absorption spectra of thyroxin, tryptophan, and 2-hydroxyindole-3-propionic acid reveals a definite "family" resemblance. There are present in all three spectra two chief bands, thyroxin showing a small but definite band at 2750 Å.U. Table I shows the comparative relationships of the two bands. The "head" of a band represents the point of maximum absorption, the "base" the point of least absorption, the difference between the coefficients of these two points being the "persistence" of the band.

TABLE I.

	Band in the region 2500—3300 Å.U.				Band in the region 2100—2300 Å.U.	
Substance.	Ext. coef. of head × 10^{-4}.	Wave-length. Å.U.	Ext. coef. of base × 10^{-4}.	Wave-length. of base.	Ext. coef. of head × 10^{-4}.	Wave-length.
Thyroxin	4·5	3275	2·5	2950	35	2275
Tryptophan ...	5·75	2750	0·1	2425	35	2200
2-Hydroxyindole 3-propionic acid	5·6	2500	0·2	2280	24	2140

With regard to the region 2500—3300 Å.U., the absorption coefficients are of the same order of magnitude, and the bands occur in the same region of the spectrum within 700 Å.U. In thyroxin, as might be expected, the bands are shifted more towards the red, and the persistence of the band is diminished, although to an extent apparently greater on account of the logarithmic notation used in plotting the absorption coefficients.

The band in the extreme ultra-violet has shown little shift towards the red, and the order of magnitude of the absorption coefficients is the same. In thyroxin, the iodine has undoubtedly shifted both bands, but one more than the other, the effect of "spreading" of the curve being noticed. The break in the curve at 2750 Å.U. seems to be due to a definite band, but owing to the experimental difficulties experienced in using such small amounts of material, it is not intended to attempt more than general comparisons from the results.

It would appear that there is a definite group resemblance, and that the indole type of curve as mapped by Ward (*Biochem. J.*, 1923, **17**, 6) is present in thyroxin. Owing to the measurements being pushed further into the ultra-violet, the second band, not plotted by Ward, was found to be present, first in thyroxin, and later in the other compounds studied.

Although an indoline derivative, the effect of substitution of iodine in the molecule, on the bands, is of interest, showing, but to a less degree, the effect first indicated by Hartley (J., 1881, **39**, 165; 1885, **47**, 693; 1903, **83**, 244), namely, a shift towards the red. The band at 4200 Å.U. moves to 4400 Å.U. and the extinction coefficient is reduced slightly. The band at 2400 Å.U. moves to 2500 Å.U., whilst that at 3000 Å.U. moves to 3075 Å.U., its persistence being at the same time reduced (compare thyroxin). The curve is spread, and all the effects seen in thyroxin are demonstrated, though to a lesser degree. Although considered by Ward to show no relation to the indole type of curve, the isatin curve does, between 3500 Å.U. and 2500 Å.U., bear a definite similarity, both in absorption coefficient and in wave-length.

Derivatives of tryptophan and thyroxin are now being studied, with a view to complete this survey, and to elucidate the formation of the "open ring" form of thyroxin postulated by Kendall (*J. Biol. Chem.*, 1919, **40**, 284), as well as to determine whether the reduced ring type of compound will give the indole type of curve.

Summary.

(1) The primary object of the investigation was to ascertain what relation, if any, exists between tryptophan and thyroxin.

(2) The absorption curves for these substances are related sufficiently to warrant the conclusion that the indole skeleton is present in thyroxin.

(3) Whether the indole type of curve will persist when the benzene ring portion of the molecule is reduced is to be further determined.

I have to thank Professor Sir F. Gowland Hopkins for placing the necessary apparatus at my disposal, and for his interest and advice during the research of which this forms a part. I am also indebted to Dr. E. C. Kendall, of the Mayo Foundation, for the specimen of 2-hydroxyindole-3-propionic acid used in the investigation, which has been conducted during the tenure of a Beit Memorial Fellowship for Medical Research.

THE UNIVERSITY, CAMBRIDGE. [*Received, January 26th*, 1925.]

CX.—*The Effect of Colloids in the Displacement of Lead and Copper from their Salts by Zinc.*

By LEONARD THOMAS MILLER GRAY.

ALTHOUGH the influence of addition agents in electro-plating has been the subject of many investigations, only one reference to the effect of colloids on the chemical replacement of metals, apart from studies in the preparation of sols in the presence of protective colloids, has been found. Freundlich and Fischer (*Z. Elektrochem.*, 1912, 8, 885) investigated the effect of dipping a zinc rod or immersing a zinc plate in nearly saturated solutions of certain lead salts with and without the addition of 0·04% of gelatin. They concluded that the addition of gelatin gave finer crystals, and that since the solutions were neutral and nearly saturated, this effect was due rather to conditions of crystallisation than to electrical influence of a secondary kind.

It was thought that more systematic investigations on these lines might throw some light on the mechanism of the effect of colloids in electrolysis.

EXPERIMENTAL.

(1*a*) *Lead and Gelatin.*—In the first experiments strips of thin zinc foil approximately $2 \times \frac{3}{8}$ in. were suspended just below the surface of the liquid by threads, but were afterwards allowed to float on the surface. The concentration of the lead salt used (acetate) was kept very low by filling a 4 c.c. pipette with a saturated solution of the salt, the top of the pipette being just above the

surface of the water in the vessel, and allowing this to diffuse through 200 c.c. of water before it reached the zinc foil floating on the surface. All the experiments were carried out at room temperature. The deposits were tested for crystal form under the microscope (magnification 40 diameters), and for grittiness and cohesion by rubbing between the fingers (the " tenacity " of Marc, *Z. Elektrochem.*, 1912, **19**, 431). For the latter test the deposits were arranged haphazard, so as to eliminate as far as possible the personal element. The concentration of the gelatin (Nelson's No. 1) was varied from 0·005—2·0%.

The crystal structure of the deposit changed steadily from very fine needles to small nodules of increasing size as the percentage of gelatin increased from 0 to 0·3—0·4. When this proportion of gelatin was exceeded, the size of the compact nodules diminished, and the nodular structure was replaced by a branched structure, the deposit, on disintegration, closely resembling the original small needles.

The second test showed a similar maximum effect, but at a slightly lower concentration of gelatin. Beginning as a mass of tiny, closely coherent particles, an almost impalpable powder, in absence of gelatin, the deposit became steadily more gritty and less cohesive until a certain maximum was reached, beyond which the grittiness diminished until, with 1% of gelatin, the powder was as impalpable as at first. This maximum grittiness was attained, in four series of experiments, at almost exactly the same concentration of gelatin, 0·25—0·3%.

The term " nodules " is used to denote irregular particles, usually recognisable as aggregations of crystals, differing little in length and breadth. " Cohesion " is used to express the tendency of the discrete particles to cohere, a tendency which was quite overcome by rubbing between the fingers, so that an impalpable powder is frequently strongly cohesive, whereas the most gritty specimens are like grains of sand, with no cohesion between the grains.

(1*b*) *Lead and Gum Arabic.*—Two series of experiments were carried out, the concentration of gum being varied from 0—10%, but no maximum effect was observed. The grittiness increased steadily with increasing concentration up to 2% of gum, while no deposit was obtained on any of the strips in solutions with over 2% of gum, even after 6 weeks' contact. These solutions of higher concentration very rapidly became mouldy.

(1*c*) *Lead and Glue.*—A very strong Scotch glue was used, the solution of which in water reacted faintly acid to litmus. Two series were carried out, with almost identical results. The maximum grittiness was obtained with 0·6% of glue, and two distinct changes

of crystal structure were observed. The first took place between 0·02% and 0·05% of glue; at the lower concentration the structure still showed the needles of the pure solution, but at the higher concentration these had almost entirely given place to small nodules and branched fern structures. As the concentration of glue increased, the nodules joined together to form larger aggregations, reaching a maximum at 0·6%, the point of maximum grittiness, after which the aggregations steadily became smaller.

(2*a*) *Copper and Gelatin.*—A saturated solution of copper sulphate was used in the pipette, while the concentration of gelatin was varied from 0·002—1·0%. Three series were carried out, but the results in general were rather irregular owing to the fact that under these conditions copper is much more tenaciously deposited on a zinc strip than is lead, so that in many cases the tests for grittiness could not be made. A distinct maximum was, however, found, both for grittiness and for size of aggregates, at 0·15, 0·15, and 0·2% of gelatin respectively, in the three series.

(2*b*) *Copper and Glue.*—In all the previous experiments the zinc strip was in contact with the salt solution for periods of 20 to 45 days, sufficient metal for testing purposes then being at the bottom of the vessel. In this case, after 60 days, almost all the deposit clung tenaciously to the zinc strip. The test for grittiness had therefore to be abandoned and the copper deposit was examined on the zinc strip itself. The method of experiment was changed and the strip left for only a few days in contact with the solution. The rate of diffusion of copper sulphate from the pipette, and therefore the concentration of the salt, had a very marked effect on the nature of the deposit, so the pipettes were abandoned and the copper sulphate was added directly to the liquid to give a known concentration. As the strip frequently became incrusted with a deposit, turquoise blue or white (presumably basic salts), boric acid was added to the solution, with satisfactory results. The object of this series now became the production of the best deposit of smooth bright copper on the strip, this being judged by the naked eye and by the effect of burnishing.

Influence of concentration of copper sulphate. This was varied from 0·0002—0·0069*M*. The lower concentrations gave a closely adherent film, usually brownish-black, but frequently having a pink tinge. At the highest concentrations the film was similar in colour, but not so adherent, while the edges of the strip were incrusted with large globules of black copper. Strongly adherent films of bright copper were obtained with concentrations of 0·0020—0·0026*M*. These could be burnished and took a high polish.

Influence of concentration of glue. The concentration of copper

sulphate producing the best deposit was apparently independent of the concentration of glue and of other factors, but the concentration of glue required to give the best deposit varied considerably with the other factors. The glue solution when freshly prepared was very sensitive, and was readily coagulated by the copper sulphate. This sensitiveness usually disappeared on ageing for 24 hours, but the solutions coagulated at once if kept at too high a temperature, say above 25°. The concentration required to give the best deposit varied with the time of contact; *e.g.*, in a series of experiments under exactly the same conditions the best deposit was obtained after 2 days with 1·05% of glue, after 4 days with 1·2%, and after 14 days with 1·5%. Of these three deposits, that obtained after 4 days was the best on burnishing. In all cases there was a distinct deterioration in the deposit after 10 days' contact with the solution.

In general, a loose, dark deposit was obtained at low concentrations of glue. The brightness and tenacity attained a maximum at a concentration of glue varying from 0·6% to 1·5% according to the time of contact, size of zinc strip, etc.; the brightness then decreased steadily, but not the tenacity.

Influence of boric acid. The best deposits were obtained with 0·6—0·8% of boric acid, becoming distinctly poorer as the concentration approached 1%.

Influence of zinc strip. Mechanical cleaning with fine emery paper gave better results than treatment with acid or alkali. With large strips, the best deposit was produced at a smaller concentration of glue than with small strips, other conditions being the same.

Discussion.

Investigators of the influence of addition agents in electrolysis have as a rule noted no such maximum effect as has now been described, but most of their experiments were prolonged only until further addition of colloid ceased to be beneficial, and not until further addition became actually detrimental. Kern (*Trans. Amer. Electrochem. Soc.*, 1920, **38**, 143) found a maximum when using gelatin in the refining of tin. The fact that gum arabic shows no such maximum is in accord with the results of Isgarischev (*Koll. Chem. Beihefte*, 1921, **14**, 25), who showed that a maximum increase of polarisation is given by 0·025% of gelatin and by 2% of gum arabic, these figures being approximately in the same relation as the respective gold numbers. Since there is a close connexion between the protective effect of colloids and the increase of polarisation (Marc, *loc. cit.*, and other investigators), gum arabic might

be expected to show a maximum in these experiments at about 20%, *i.e.*, above the experimental limits.

The generally accepted effects of colloids in electrolysis are decrease of (*a*) crystal size and (*b*) cohesive power. In these experiments with lead the size of the component crystals apparently diminishes fairly steadily throughout, but the cohesive power, by which these crystals form larger aggregates, increases up to a certain point and then diminishes. Now, it is quite conceivable that a very thinly adsorbed film of colloid may exercise a certain cohesive power, whereas when the colloid concentration is higher this film becomes thicker, and is a source of weakness and not of strength in the aggregate.

In the copper experiments with glue, the decrease in size is apparently the decisive factor. The deterioration of the deposit with time of contact would then be due to the continued adsorption of colloid on the surface of the copper crystals after the zinc strip has been covered by copper, and the chemical action practically stopped. With a higher concentration of glue the whole process would be slower and the deposit would contain a higher proportion of adsorbed colloid.

Since Isgarischev (*loc. cit.*) detected a change in the viscosity curve of his solutions corresponding to the critical concentration of gelatin, a number of viscosity experiments were made. The curves obtained were quite smooth. There is therefore no indication of the formation of compounds between colloid and ions.

I desire to express my thanks to Professor A. J. Allmand for suggesting this research and for his constant help and advice during its course.

UNIVERSITY OF LONDON,
KING'S COLLEGE. [*Received, February 2nd*, 1925.]

CXI.—*The Surface Tensions of Aqueous Phenol Solutions. Part I. Saturated Solutions.*

By ARTHUR KENNETH GOARD and ERIC KEIGHTLEY RIDEAL.

The Drop-weight Method of Determining Surface Tension.

THE theoretical formula for the maximum weight of a cylindrical drop hanging from a tube, in equilibrium, is

$$W = \pi r \sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where W = the weight of the drop, r = the radius of the tube, and σ = the surface tension (compare Worthington, *Proc. Roy. Soc.*,

1881, **32**, 362; *Phil. Mag.*, 1884, 1885, and Rayleigh, *Phil. Mag.*, 1899, **48**, 321).

If the detachment of the drop be considered to follow immediately, this formula would lead to the result that, *ceteris paribus*, W is proportional to r, a "law" previously discovered empirically by Tate (*ibid.*, 1864, **27**, 176). Rayleigh, however, showed (*loc. cit.*) that in practice equation (1) has to be modified; π has the value 3·8, as an approximation, for tubes of moderate radius; if r be either very small or very large, the "constant" rises well above 4; it is nowhere strictly constant.

This variation is of course due to the fact that the actual detachment of the drop is an extremely complex dynamical process (compare Perrot, *J. Chim. phys.*, 1917, **15**, 164). An attempt to derive an adequate theoretical formula has been made by Löhnstein (*Z. physikal. Chem.*, 1908, **64**, 686), but his results cannot be said to be entirely satisfactory. On the other hand, Morgan and his co-workers (*J. Amer. Chem. Soc.*, 1908—1913) have published a large number of papers in support of "Tate's Laws," claiming that under suitable conditions $W = Kr\sigma$, where K is a constant. This view, however, cannot be substantiated.

An empirical correction curve has been determined by Harkins and his co-workers (*ibid.*, 1916—1922), who have compared the surface tensions, measured by the capillary rise method, with the drop weights of water and other liquids, using dropping tubes of varying bores. The experiments, which are virtually repetitions of those of Rayleigh under improved conditions and over a greater range, are probably very accurate, but the theoretical portions of Harkins's papers leave something to be desired. For example, the relation between surface tension and drop-weight [using the same notation as in (1) above] is expressed by the equation

$$W = 2\pi r\sigma\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ϕ is the empirical correction factor. A drop for which ϕ is unity is called by Harkins an "ideal drop." This term is open to the objection that equation (2) has no meaning whatsoever, theoretical or practical.

A return to a more rational expression of the relation between drop-weight and surface tension has been made by Iredale (*Phil. Mag.*, 1923, **45**, 1088). This expression rests on the fact that different liquids may form drops of similar shape from tubes of different diameters. From this, and from the assumption that rupture occurs at the point of maximum concavity, the equation

$$K_2 = \sigma_1\rho_2/\sigma_2\rho_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is developed, where σ_1, σ_2, and ρ_1, ρ_2 are the surface tensions and

densities, respectively, of two liquids and K_2 is the ratio of the radii of the tubes from which they hang. All that is required for the practical determination of surface tension from this formula " is a knowledge of the tube-radius and drop-radius ratio, with a continuously varying radius of tube, for some standard liquid of known surface tension and density " (Iredale, *loc. cit.*).

The method of evaluation, and the table of values calculated from the data of Harkins and Brown given by Iredale have been employed by us.

In the second of two papers published in 1907, Antonov (*J. Chim. phys.*, 1907, **5**, 372) laid down the following rule:

" If A and B be two partially miscible liquids, the surface tension at the surface of contact of the two equilibrium liquid layers is equal to the surface tension of A saturated with B, less the surface tension of B saturated with A."

Data confirming this rule were given for three systems: water and (*a*) *iso*butyric acid, (*b*) ether, (*c*) benzene. The only other paper bearing on Antonov's rule seems to be one published by Reynolds (J., 1921, **119**, 466), who studied six systems: water and (*b*) ether, (*c*) benzene, (*d*) chloroform, (*e*) carbon tetrachloride, (*f*) nitrobenzene, (*g*) aniline. The rule is restated by Reynolds as a result of his observations, though no reference is made to its original author. We may take it that it is proved, at least to a first approximation, although the experiments quoted are not of a very high order of accuracy.

The system phenol–water has been studied by Whatmough (*Z. physikal. Chem.*, 1902, **39**, 129) and by Morgan and Evans (*J. Amer. Chem. Soc.*, 1917, **39**, 2151). Here the interfacial surface tension is so small that it is difficult, if not impossible, to determine it directly. Work has therefore been confined to the determination of the surface tensions of the two liquid phases; in Morgan's paper, Antonov's rule is more or less tacitly assumed.

Whatmough studied the surface tensions of the two phases from room temperature to the critical solution point; he found that the difference of surface tension decreased from about 0·5 dyne/cm. at 20° to zero at the critical solution temperature; *the surface tension of the water-rich phase he found to be higher than that of the phenol-rich phase throughout.*

Morgan, on the other hand, who worked from 15° to 55°, found that the phenol-rich phase had the higher surface tension at room temperature. His surface tension–temperature curves were approximately straight lines for both phases; *instead of converging towards the critical solution temperature* (68·8°), *however, they crossed at* 40—45°, diverging again up to the highest temperature studied

(55°). Commenting on this divergence, Morgan remarks—"It is evident . . . that the region studied represents the straighter portion of a curve for both layers, and instead of diverging more and more [*i.e.*, above 45°], as would be indicated by an extrapolation from the linear equations, the values for the two layers, somewhere between 55° and 68·8°, where the change in concentration in each with the temperature has become excessive, begin to approach each other again, to meet and become identical at 68·8°." This supposed formation of a loop by the surface tension–temperature curves is unsupported by any experimental evidence; it is, of course, based on the fact that the surface tension of the two layers must become identical at the critical solution temperature.

This remarkable result does not appear to have been either confirmed or challenged. That Morgan's conclusions, and also those of Whatmough, were based on experimental error can be demonstrated by the following simple qualitative test: If a two-phase mixture of water and phenol be allowed to stand in a test-tube, it will be observed that the meniscus at the surface of separation of the two liquid phases is convex towards the water-rich phase. In other words, the angle of contact with glass made by the phenol-rich phase is greater than a right angle. If, now, a capillary tube be inserted into the mixture, of such a length that its upper end lies below the liquid–air interface, the meniscus at the liquid–liquid interface will be found to be *depressed* in the capillary tube below the level of the interface outside the capillary. The interfacial tension is small, but owing to the small density difference between the two phases, the depression is considerable. This experiment was performed by us at six different temperatures ranging from 20° to 66°, with a similar result in each case. It follows, therefore, that the surface tension of the phenol-rich phase is greater than that of the water-rich phase at all temperatures from room temperature up to the critical solution point; and that Morgan's "inversion point" does not exist. These results were fully confirmed by the following quantitative measurements.

Experimental.

The drop-weight apparatus employed was that described by Bircumshaw (J., 1922, **121**, 887), the radius of the tube being 0·32161 cm. Instead of the method of "blank drops," the receiving vessel, containing a little of the liquid under investigation, was weighed before each experiment, the vessel being closed with a glass stopper. This method was employed by Morgan and was quite satisfactory. Loss of weight through evaporation was estimated by blank experiments.

The Surface Tension of Pure Water.

The values 0·9148, 0·9146 g., corrected for evaporation, for the weight of ten drops of water were obtained at 20°. With a tip of the radius mentioned, it may be calculated that Harkins would have obtained the value 0·9113 g. Thinking that this difference might be due to too rapid dropping (although our average rate was similar to that recorded by Harkins), we made an experiment in which more than 30 minutes were taken to form 10 drops. The weight obtained was 0·9120 g.; owing, however, to excessively long immersion in the thermostat, the extra loss from evaporation became considerable, a blank experiment showing this to be about 0·002 g., thus bringing the true weight practically up to the former values. The surface tension, calculated from these results by Iredale's method, is 73·06 dynes/cm. instead of 72·80. Harkins, in the preparation of his water, was very careful to avoid saline impurities; but these have a very small effect (*e.g.*, to raise the surface tension of water by 0·2 dyne/cm. the salt concentration would have to be of the order of $N/10$) compared with the possible *lowering* of surface tension by grease contamination. However clean containing vessels may be, pouring water into and from them in the air is quite sufficient to cause considerable contamination. In the authors' experiments, a column of distilled water was stored for some days in a vessel from which the water was liberated at the bottom, ensuring freedom from grease, since the latter rises to the upper portion of the column on standing. This probably accounts for the slightly higher value of the surface tension obtained. This does not preclude the probability of Harkins's results being correct among themselves; all that is necessary in calculating values from Iredale's table is the assumption that Harkins employed throughout a standard liquid of surface tension 72·800 dynes/cm.

The Surface Tension of Phenol Solutions.

The surface tensions against air saturated with vapour of the two liquid phases of the phenol–water system were determined at 0°, 17°, 30°, and 40°. Pure medical phenol was used. Certain special experimental difficulties were encountered, which will be briefly described, since the unsatisfactory results of previous workers were probably due to faulty procedure. In Morgan's experiments, for example, the containing vessel held both phases, being raised or lowered in order to measure the surface tension of lower and upper phases, respectively. This is undesirable, for reasons which will be apparent.

The persistency of emulsions in the aqueous layer has been observed by all who have worked with this system. If a sufficient

volume of both phases be taken, however, the upper portion of the aqueous layer becomes clear after some hours, the emulsion sinking towards the surface of separation. The following procedure was therefore adopted :

(1) At 0°. A glass-stoppered bottle containing about 100 c.c. of each phase was immersed in a bath of melting ice, and shaken thoroughly at short intervals for some hours. It was surrounded with melting ice and kept over-night in an ice-box. Some of the two layers was then removed by means of a pipette, cleaned and dried before each operation. By closing the upper end of the pipette with the finger, and warming the middle of it with the hand, it was possible to ensure that none of the upper layer of liquid entered the pipette during its insertion into the bottle.

The liquids thus separated were transferred to stoppered bottles, and could then be introduced separately into the drop-weight apparatus, which was immersed in a large glass tank filled with melting ice, stirred vigorously.

(2) At 17°. The procedure was similar, except that a thermostat was employed instead of an ice-bath.

(3) At 30° and 40°. A thermostat was employed; at these temperatures the operations of saturation and transference of the layers to stoppered bottles could be completed in one day. An important difficulty arose during the determination of the surface tension of the phenol-rich phase at 40°. Owing to the fact that the liquid was unavoidably cooled somewhat during the setting up of the apparatus, separation occurred. The aqueous phase which separated, having the lower surface tension, tended to line the inner surface of the capillary tube, and traces of it could not be removed by drawing the liquid backwards and forwards through the tube. It was found necessary to clean and dry the capillary tube before each experiment, and to warm the phenol-rich phase in the containing cup above 40° before placing it in position and immersing the whole apparatus in the thermostat. By this means separation of the aqueous phase was avoided, and measurements could be taken as soon as the liquid in the containing cup had cooled to 40°.

The densities of the two phases were determined by means of a pyknometer. Three determinations of the weights of twenty drops were made with each phase at each temperature; two typical results are given below :

	Wt. (g.) of 20 drops.	Max. diff. (g.).
Temp. 0°. Water-rich phase	1·0249, 1·0249, 1·0229	0·0020
Temp. 17°. Phenol-rich phase	0·9979, 0·9979, 0·9985	0·0007

At 40° the variation from the mean value amounted to $\pm$ 0·15%; owing to the very small difference between the drop weights of

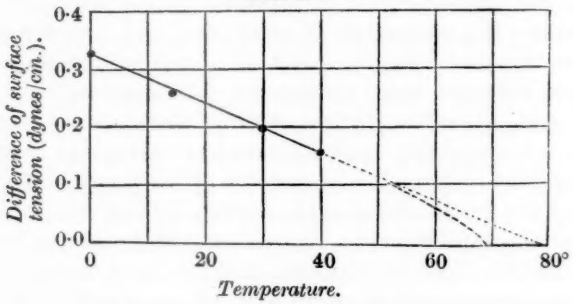
the two phases, it was not practicable to work at temperatures higher than this.

The following table gives the results, the drop weights being corrected for evaporation.

Temp.	Phase.	Density.	Mean drop-wt. (g.).	Surface tension (dynes/cm.).
0°	(*a*) Phenol-rich	1·9685	0·05162	41·81
,,	(*b*) Water-rich	1·0085	0·05122	41·48
17	(*a*)	1·0537	0·04995	40·45
,,	(*b*)	1·0060	0·04963	40·19
30	(*a*)	1·0442	0·04877	39·50
,,	(*b*)	1·0025	0·04852	39·30
40	(*a*)	1·0332	0·04802	38·91
,,	(*b*)	0·9990	0·04782	38·75

The surface tension–temperature curves are convex towards the temperature axis, the convexity increasing somewhat as the temperature rises. The differences between the surface tensions of the two phases are shown in the accompanying curve, plotted against temperature. It is evident that extrapolation of the curve would give zero difference of surface tension somewhere between 60° and 80°.

FIG. 1.



The results therefore confirm quantitatively those of the qualitative experiment previously described, and indicate that there is no point below the critical solution temperature at which the difference of surface tension becomes zero.

Comparison with other Systems.

There appears to be a general relation between the difference of surface tension between two such phases and their tendency towards complete miscibility. The following data illustrate this point :

Systems Water and	Diff. between S.T. of two phases.	Temp. of complete miscibility.	
Benzene	34·4 dynes/cm.	?	Reynolds
Nitrobenzene	24·7 ,,	?	
Aniline	4·2 ,,	167°	
Phenol.....	0·26 (17°)	68·8	Goard and Rideal

The phenol–water system is remarkable, as the phase richer in the low-tension component has the higher surface tension.

Summary.

(1) The history of the drop-weight method of determining surface tension has been briefly discussed and reasons have been given for adopting the method of calculation proposed by Iredale. The value 73·06 dynes/cm. is obtained for the surface tension of water at 20°.

(2) Experiments have been described upon the surface tensions of the two liquid phases formed by water and phenol at four different temperatures. The difference between the surface tensions of the two phases has been shown, by quantitative measurements up to 40°, and by qualitative experiments at higher temperatures, to diminish regularly up to the critical solution temperature. Previous results by other workers have thus been proved incorrect. No "inversion point" at 40—45° would appear to exist.

(3) The difference between the surface tensions of phases of this type seems to decrease with the tendency of the two liquids forming them to become completely miscible.

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CXII.—*The Photosensitive Formation of Water from its Elements in the Presence of Chlorine.*

By RONALD GEORGE WREYFORD NORRISH and ERIC KEIGHTLEY RIDEAL.

IN recent years the photochemical reaction between hydrogen and chlorine has received much attention from physical chemists, and as a result accurate data have now accumulated which enable a tolerably complete theory of this complicated reaction to be established. In general, it has been found that the presence of impurities exerts a very marked influence on the course of the reaction, manifesting itself in the period of induction, originally discovered by Bunsen and Roscoe (*Phil. Trans.*, 1857, **147**, 381), and thought by them to be a primary attribute of the reaction. Distinct from the action of foreign substances in producing the induction period, is the anticatalytic effect of oxygen, which has been shown to be related in a very simple way with the oxygen concentration both by Bodenstein and Dux (*Z. physikal. Chem.*, 1913, **85**, 297) and by Chapman and MacMahon (J., 1909, **95**

135). They have shown that the velocity of hydrogen chloride formation is inversely proportional to the concentration of oxygen, or $d[HCl]/dt = k/[O_2]$, for constant pressures of hydrogen and chlorine. It was early thought that this action of oxygen was to be attributed to some property it possessed of deactivating chlorine molecules excited by the absorption of radiation (Chapman and Underhill, J., 1913, **103**, 496), but no mechanism was postulated until M. C. C. and D. L. Chapman suggested (J., 1923, **123**, 3062) that it was connected with the formation of water. As long ago as 1907 Weigert (*Ann. Physik*, **24**, 55, 243) had shown qualitatively that a large quantity of water is produced when a mixture of hydrogen, chlorine, and oxygen is exposed to visible radiation, and it seems curious that no one had connected this fact with the anti-catalytic effect of oxygen upon the hydrogen chloride reaction. It occurred to the present authors that such a connexion must exist, and the research described in this paper has been carried out in order to obtain quantitative information upon the reaction of Weigert, with a view to discovering the mechanism, and tracing its connexion, if any, with the kinetics of hydrogen chloride formation.

By means of the apparatus described below, it was possible to bring hydrogen, chlorine, and oxygen in any desired proportions into a reaction tube containing phosphorus pentoxide in a thermostat, and the rate of formation of water, upon illumination of the mixture by visible radiation only, could be measured by observing the rate of change of gaseous pressure as the water formed was absorbed. The total pressure of the reactant gases was maintained initially at 70 cm. of mercury, and, under the most favourable conditions of water formation, fell by about 3 cm. of mercury in 30 minutes, so that the reaction was virtually carried out at constant pressure. The rate of formation of water was independent of hydrogen pressure over the very wide range investigated, *i.e.*, from 0·16 to 0·9 of the total pressure, and was proportional to the product of the chlorine and oxygen concentrations, or

$$d[H_2O]/dt = k[O_2][Cl_2].$$

In this respect, the mechanics of the reaction are similar to the photosensitive action of chlorine upon the decomposition of ozone by visible radiation studied by Bodenstein and Bonhoeffer (*Z. Physik*, 1923, **13**, 94), who found that the velocity of decomposition was given by the relationship $-d[O_3]/dt = k[O_3][Cl_2]$.

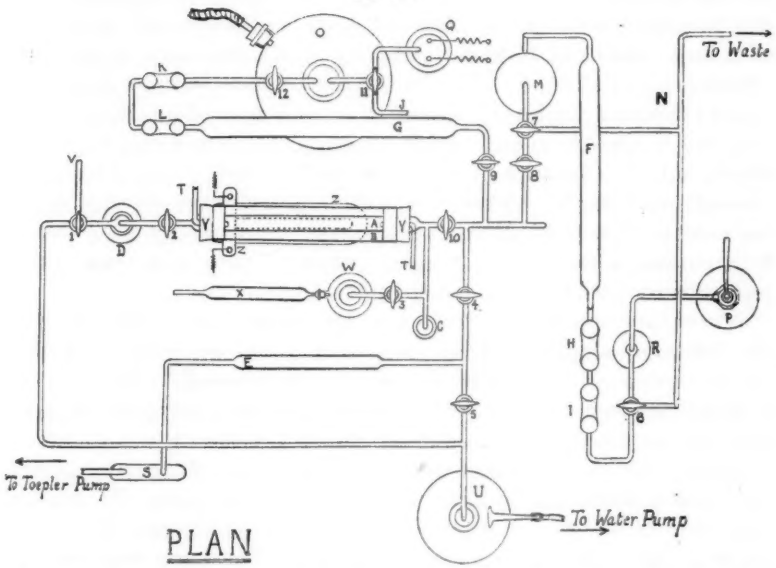
Both these expressions are consistent with the hypothesis that the reactions in question are brought about by the catalytic influence of chlorine molecules activated by radiation, and thus, together with the activation of hydrogen by resonating mercury atoms, discovered by Cario and Franck (*ibid.*, 1922, **21**, 161), these reactions may be

classed as the simplest cases of photochemical sensitisation. They are possibly comparable with the numerous cases of optical sensitisation of the photographic plate produced by impregnation of the silver salts with organic dyestuffs.

EXPERIMENTAL.

The reaction chamber (Fig. 1) consisted of a glass tube, A, 34 cm. long, 2 cm. in internal diameter, and of about 100 c.c. capacity, which had been carefully cleaned with chromic acid and distilled water, and dried. A small quantity of phosphoric acid was placed

FIG. 1.



along the bottom of the tube. The reaction tube was jacketed by a wide tube, B, 5 cm. in diameter, and the rubber stoppers, Y, Y. A rapid stream of water was circulated through this outer tube from a thermostat by way of the tubes S, T, by means of a pump. A preliminary evacuation of the reaction tube could be effected by opening taps 10, 4, and 5, thus effecting communication with a water-pump. The evacuation could then be completed after closing 5, by means of a Toepler mercury pump, which communicated with the apparatus through a tube, E, containing caustic soda, and finally closing tap 10. The hydrogen–oxygen mixture was prepared by adding either pure hydrogen or oxygen to electrolytic gas, and was stored in the aspirator, O. By opening taps 12 and 9, and then 10 very carefully, the mixture was passed into A,

by way of the U tubes K, L, containing soda-lime and calcium chloride respectively, and the tube G, containing phosphoric oxide sprinkled on glass wool. When the required partial pressures of hydrogen and oxygen had been obtained in A, as registered by the vertical mercury manometer, C, the connecting tube between taps 10, 9, 8, and 4 was re-evacuated by the water-pump by opening 5 and 4. This connecting tube was then filled with chlorine by shutting 4 and expanding the gas from the chlorine container, M, by way of taps 7 and 8. Evacuation and refilling with chlorine were carried out in this way three times, and then the chlorine in the container M was allowed to expand by way of taps 7, 8, and 10 into A until a total pressure of 700—720 mm. was registered on the mercury manometer. The chlorine container, M, consisted of a large vessel of 1500 c.c. capacity which was kept filled with chlorine by allowing a constant stream to flow through from the liquid chlorine cylinder, P, by way of the water bubbler, R, the two-way tap 6, the U tubes I and H (containing calcium chloride), the drying tube F (containing phosphoric oxide), the tap 7, and to waste through the tube N. When it was desired to use the chlorine in M, the stream from the cylinder was diverted to waste by turning tap 6 in communication with N, and putting 7 into communication, *via* 8 and 10, with the reaction chamber.

When these conditions for filling the tubes were observed, *i.e.*, the chlorine being put in last, the mercury in the vertical manometer, C, was not affected by the chlorine for generally over an hour, it being protected by a layer of hydrogen and oxygen. A new mercury manometer was fused on for each experiment.

During the preparation of the required mixture of the three gases, the double-barrelled, quartz mercury vapour lamp, Z, placed vertically below A and effectively screened, was allowed to run in order to get to a steady state of burning. The lamp was worked off a 220 volt circuit and carried a current of 4·5 amps. Its distance from the reaction chamber was kept constant at 8 cm. below the outer tube, B.

By moving the screen between the lamp and the tube B, the mixture of gases in A could be exposed directly to the visible radiation of the quartz lamp, the ultra-violet radiation being absorbed by the glass walls of the vessels A and B. The first effect observable upon illumination was an immediate increase of pressure occasioned by the Draper effect, which seemed roughly to be proportional in magnitude to the square of the chlorine concentration. After about $\frac{1}{4}$ minute, the pressure began to fall off, and after 1 or 2 minutes the rate of decrease became regular as the water formed was absorbed by the phosphoric oxide.

Two series of preliminary experiments were carried out in order to ensure that no reduction of pressure occurred through the absorption of hydrogen chloride by the dry phosphoric oxide.

In the first case, pure hydrogen and chlorine were enclosed in the reaction tube and illuminated. A preliminary expansion (Draper effect) always occurred, but no subsequent fall of pressure, showing that the hydrogen chloride formed was not appreciably absorbed. This experiment was carried out at intervals throughout the work as a test of the efficiency of the phosphoric oxide, and it was always found that so long as no moisture was observable on the phosphoric oxide no absorption of hydrogen chloride occurred. The phosphoric oxide in the reaction tube was always replaced after every four or five experiments, so that dry material was always used, although it was found in general to be efficient for some eight or nine experiments.

As a second check that no hydrogen chloride or chlorine was absorbed by the drying agent, the total combined and uncombined chlorine in the gaseous phase after illumination was estimated and compared with the quantity of chlorine initially put in, estimated from pressure–volume measurements. In these experiments electrolytic gas–chlorine mixtures were used, and a decrease of pressure due to the formation of water was always observed. The chlorine in the gaseous phase after illumination was estimated by drawing the gases out of the chamber *via* stopcocks 1 and 2 by means of the water-pump through potassium iodide solution contained in the wash-bottle, D (Fig. 1). The free chlorine liberated iodine, whilst the hydrogen chloride was dissolved, so that the total chlorine could be obtained by successive titrations with standard sodium thiosulphate and standard caustic soda. From the following figures (Table I), it will be seen that the chlorine initially put

TABLE I.

Volume of reaction chamber = 110 *c.c.*

Pressure of electrolytic gas in mm. of Hg.	Pressure of chlorine in mm. of Hg.	Chlorine (g.) estimated at end of exposure. (*a*) As HCl.	(*b*) As Cl_2.	Total Cl (g.) estimated at end.	Total Cl_2 (g.) put in initially.	Diff (g.).
688·5	30·3	0·00924	0·00248	0·0117	0·0129	−0·0012
649	78	0·0264	0·00603	0·0325	0·0334	−0·0009
582	128	0·0480	0·0073	0·0553	0·0553	0·0000
456	250	0·0970	0·0122	0·1092	0·1075	+0·0017
277·5	414·5	0·0618	0·1183	0·1801	0·1775	+0·0026

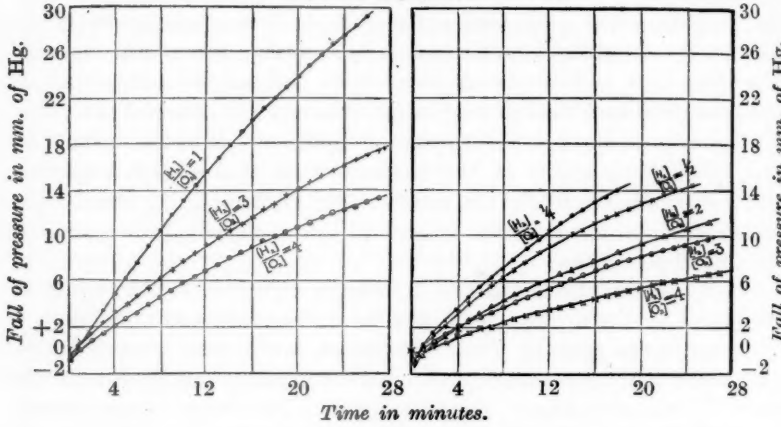
into the reaction chamber can be accounted for at the end within the accuracy of the experimental method, proving that no appre-

ciable absorption of either hydrogen chloride or chlorine by the drying agent occurs under the conditions obtaining in these experiments.*

FIG. 2. *Pressure of* Cl_2 *=ca. 110 mm.*

FIG. 3. *Pressure of* Cl_2 *=ca. 55 mm.*

Total pressure of gases=700 mm.



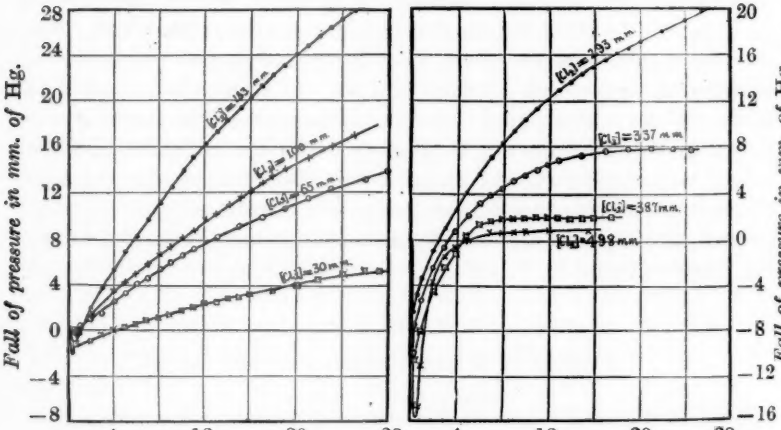


FIG. 4. *Medium and low pressures of chlorine.* $[H_2]/[O_2]=2$.

FIG. 5. *High pressures of chlorine.* $[H_2]/[O_2]=2$. *Large Draper effects.*

Time in minutes.

Even if the small irregular differences shown in the last column are real, they yield, when put in terms of pressure change, figures

* For pressures of hydrogen chloride of 500 mm., a small decrease in volume was observed after 24 hours' contact with phosphorus pentoxide.

which are small compared with the actual pressure change recorded due to water formation, and in general do not vitiate the results by more than $\pm 5\%$. It is believed, however, that the pressure change observed gives the water formation to a closer degree of accuracy than this, since it has already been shown above independently that hydrogen chloride or chlorine absorption does not take place under the present conditions of experiment.

These preliminary experiments having established this fact, a large number of experiments were carried out with hydrogen and oxygen in ratios ranging from 4 to $\frac{1}{4}$ and chlorine in varying proportions. A large number of curves, of which those in Figs. 2 to 5 are characteristic, were obtained, in which fall of pressure is plotted against time in minutes. These curves show, in nearly all cases, a preliminary increase in pressure due to the Draper effect, which lasted for about 1 minute, and thereafter a regular fall in pressure due to the absorption of the water produced. The rate of fall of pressure gradually decreases as the reaction proceeds to completion, but by taking the initial slope of the curves after the first 2 minutes, when the system has recovered from the Draper effect, we obtain a measure of the rate of formation of water. This slope is defined as the " water sensitivity " of the reaction mixture and is directly proportional to the initial rate of formation of water. In general, the slope could be determined very accurately, since for several minutes after the start the rate of fall of pressure remained uniform.

In the cases where the chlorine pressure is large, the Draper effect is very great, since the velocity of hydrogen chloride formation to which this is proportional (Baly and Barker, J., 1921, **119**, 653) depends roughly on the square of the chlorine concentration. If at the same time the hydrogen pressure is small, the hydrogen will be rapidly used up, so that at the time the system has recovered from the Draper effect, the hydrogen pressure will be very largely reduced. For such cases (indicated by an asterisk in the tables and shown in Fig. 5), no accurate estimate of the water sensitivity can be obtained, as the pressure changes too rapidly, and the reaction is over too quickly to enable any photochemical stationary state to be established in the system.

The figures in Table II embodying the results of these experiments indicate that the water sensitivity is proportional to the product of the chlorine and oxygen concentrations, and independent of the hydrogen concentration over a wide range of hydrogen pressures, as is shown by the constancy of the figures in the last column.

TABLE II.

Ratio $[H_2]/[O_2]$.	Pressure of reactant gases in mm. of mercury. Chlorine.	Oxygen.	Hydrogen.	Total.	Product $[Cl_2][O_2] \times 10^{-2}$.	Water sensitivity. S.	$K = [Cl_2][O_2]/S \times 10^{-2}$.
4	57	131·2	525	713	74·8	0·33	226
4	116·5	120	480	716	140	0·61	230
4	177·5	106·5	426	710	189	0·90	210
4	214	99·5	398	721	213	0·94	227
4	341	75·2	301	717	256	1·07	240
3	57	161	483	701	92	0·41	225
3	114	147	441	701	167	0·78	229
3	181	129	388	698	234	1·02	229
3	252	115	345	712	290	1·23	236
3	304·5	99·5	298·5	702·5	303	1·31	231
2	30·3	230	460	720	69·7	0·30	232
2	32	221	442	695	70·7	0·28	252
2	64	210	420	694	134	0·58	232
2	66	210	420	696	138	0·62	223
2	81	210	420	711	170	0·76	224
2	100	206	412	718	206	0·78	260
2	128	194	388	710	248	0·94	264
2	156·5	185·5	371	713	290	1·28	234
2	159·5	185	370	714·5	295	1·26	234
2	183	182	364	729	333	1·42	234
2	187	179	358	724	334	1·50	223
2	218·5	163	326	707·5	356	1·46	238
2	249	152	304	705	378	1·44	263
2	293·5	139	278	710·5	407	1·61	253
2	337	120	240	697	405	1·70	238
2	387·5	114	228	729·5	434	1·22 *	352 *
2	414·5	86	172	672·5	356	0·45 *	792 *
2	498·5	73	146	717·5	365	0·38 *	960 *
1	46·5	332·5	332·5	731·5	155	0·65	237
1	107·0	307·5	307·5	722	329	1·41	233
1	163·5	278	278	729·5	455	1·90	237
1	204·5	256	256	716·5	524	2·17	241
1	254	233	233	720	592	2·14	276
½	50	445	222	717	222	0·92	241
½	51	449	225	715	229	0·94	243
½	57	449	224	730	226	0·90	250
½	112	409	205	726	458	1·64	279
½	170	365	183	718	621	1·58 *	393 *
½	240	319	160	719	768	1·73 *	444 *
⅓	35·5	511	170	716·5	181	0·62	292
⅓	70·0	493	164	727	345	1·21	285
⅓	100	451·5	150·5	702	451	1·60	282
⅓	166·5	416	139	721·5	692	1·36*	509 *
¼	28	542	135·5	705·5	152	0·56	272
¼	37	542	135·5	716·5	201	0·68	295
¼	51	529	132	712	270	0·98	275
¼	52	532	133	717	263	1·00	263
¼	69·5	511	128	708·5	357	1·22	292
¼	98	493	123	714	482	1·51	313
¼	106	488	122	716	517	1·69	305
¼	149	451	113	713	672	1·30 *	517 *
¼	149	451	113	713	674	1·32 *	510 *
¼	209	404	101	714	845	1·38 *	612 *

Discussion of Results.

A simple explanation of the photosensitive action of chlorine may be obtained by means of the hypothesis that chlorine molecules activated by the absorption of radiation can transfer some of their intra-atomic energy to oxygen molecules upon collision with them, thereby rendering the latter active and capable of reacting with hydrogen molecules to form water.

Let us represent the concentration of active chlorine at any moment by $[Cl_\epsilon]$. The rate of formation of these active chlorine molecules is proportional to the intensity of illumination and to the chlorine pressure, *i.e.*,

$$d[Cl_\epsilon]/dt = kI[Cl_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

There are two possible modes of their reversion to the non-active state :

(1) Degradation of their energy by thermal radiation.

(2) Degradation by collision with oxygen molecules and activation of the latter.

The active chlorine molecules may also be removed from the sphere of action by

(3) colliding with hydrogen molecules and forming hydrogen chloride.

(4) colliding with chlorine molecules and forming dissociated chlorine atoms capable of starting " Nernst chain reactions."

For their rate of removal, we may thus write :

$$+ d[Cl_\epsilon]/dt = k_1[Cl_\epsilon] + k_2[Cl_\epsilon][O_2] + k_3[Cl_\epsilon][H_2] + k_4[Cl_\epsilon][Cl_2] \quad (2)$$

Equating equations (1) and (2) we obtain the equilibrium quantity of active chlorine present at any moment :

$$[Cl_\epsilon] = \frac{kI[Cl_2]}{k_1 + k_2[O_2] + k_3[H_2] + k_4[Cl_2]} \quad . \quad . \quad . \quad (3)$$

Denoting by $[O_\epsilon]$ the concentration of active oxygen molecules, the rate of oxygen activation is, according to hypothesis :

$$\frac{d[O_\epsilon]}{dt} = k_2[Cl_\epsilon][O_2] = \frac{kk_2I[Cl_2][O_2]}{k_1 + k_2[O_2] + [k_3][H_2] + k_4[Cl_2]} \quad . \quad . \quad (4)$$

The activated oxygen molecules may be removed either

(1) by thermal degradation of their energy

or (2) by the collision with hydrogen and formation of water.

We may thus write :

$$+ d[O_\epsilon]/dt = k_5[O_\epsilon] + k_6[H_2][O_\epsilon] \quad . \quad . \quad . \quad . \quad (5)$$

Equating equations (4) and (5), we obtain the concentration of active oxygen present at equilibrium :

$$[O_\epsilon] = \frac{kk_2I[Cl_2][O_2]}{k_1 + k_2[O_2] + k_3[H_2] + k_4[Cl_2]} \cdot \frac{1}{k_5 + k_6[H_2]} \quad . \quad . \quad (6)$$

The rate of formation of water according to hypothesis is :

$$d[H_2O]/dt = k_6[H_2][O_\epsilon] \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Hence, combining (6) and (7),

$$\frac{d[H_2O]}{dt} = \frac{kk_2k_6I[Cl_2][O_2]}{k_1 + k_2[O_2] + k_3[H_2] + k_4[Cl_2]} \cdot \frac{[H_2]}{k_5 + k_6[H_2]} \quad . \quad . \quad (8)$$

This expression reduces to that found experimentally, namely :

$$d[H_2O]/dt = k_0[Cl_2][O_2] \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

if (1) k_1 is large compared with $k_2[O_2]$, $k_3[H_2]$, and $k_4[Cl_2]$, *i.e.*, if deactivation of chlorine takes place principally by thermal degradation, and if (2) $k_6[H_2]$ is large compared with k_5, *i.e.*, if nearly every active oxygen molecule produced persists long enough to meet a hydrogen molecule and to form water.

This mechanism, which accounts for the formation of water as a result of the photosensitive action of chlorine, brings the process into line with the decomposition of ozone by illuminated chlorine, and with the activation of hydrogen molecules by excited mercury atoms referred to above.

Upon the present theory this formation of water is regarded as independent of the concomitant formation of hydrogen chloride. The anticatalytic effect of oxygen on the latter reaction is regarded as due to the direct intervention of oxygen in the hydrogen–chlorine reaction chains, a process which results in their shortening and possibly the production of water. This secondary formation of water is regarded as subsidiary to the primary formation by the photosensitive process described above, and there are good reasons for supposing that it is negligible compared with the latter.*

Summary.

The formation of water in the gaseous system hydrogen–oxygen–chlorine on illumination by visible radiation is governed by the relationship

$$d[H_2O]/dt = k[Cl_2][O_2].$$

It is independent of the partial pressure of hydrogen between the limits 0·16 and 0·9 of the total pressure. This result is consistent

* It is hoped to deal with this point in greater detail in a subsequent paper on the kinetics of the hydrogen–chlorine reaction.

with the hypothesis that activation of the oxygen is first brought about by contact with chlorine molecules activated by absorption of light.

With the photosensitive decomposition of ozone by chlorine, and the activation of hydrogen by resonating mercury atoms, this reaction falls into the simplest class of photochemical sensitisation.

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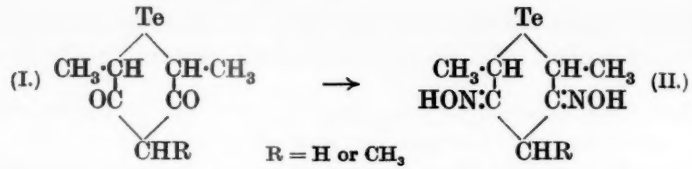
CXIII.—cyclo*Telluropentanediones Containing Aliphatic and Aromatic Substituents.*

By GILBERT T. MORGAN and CYRIL JAMES ALLAN TAYLOR.

WHEN first discovered, the tellurium derivatives containing a bivalent β-diketonic radical were regarded as cyclic compounds containing both tellurium and oxygen in the ring. Further investigation has, however, rendered this view untenable and the experiments described below confirm the hypothesis that these substances are truly organometalloidal derivatives having a six-membered ring including one tellurium and five carbon atoms (J., 1924, **125**, 1601). The two hydrogens replaced by tellurium are derived not from the methylene group but from the terminal hydrocarbon radicals.

Dipropionylmethane furnishes a bivalent chelate group to tellurium, and condensation with the tetrachloride gives rise to 2 : 6-dimethyl*cyclo*telluripentane-3 : 5-dione 1 : 1-dichloride, which on reduction yields 2 : 6-*dimethyl*cyclo*telluropentane*-3 : 5-*dione* (I). This substance under its former name of tellurium dipropionylmethane (J., 1924, **125**, 740) has been extensively employed in bacteriological studies, in which it has manifested the highest germicidal power of its series (*Biochem. J.*, 1923, **17**, 30; 1924, **18**, 190; *J. Soc. Chem. Ind.*, 1924, **43**, 304T). The diketonic structure implied by its new designation is demonstrated by the production of the *dioxime* (II).

In the tellurium condensation, dipropionylmethane reacts to a slight extent in its monoenolic form, yielding as a by-product tellurium *O*-ethyldipropionylmethane trichloride, but with 3-*methyldipropionylmethane* this tendency is inhibited and 2 : 4 : 6-*trimethyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*dichloride* becomes the only telluriferous product. On reduction, this telluridichloride furnishes 2 : 4 : 6-*trimethyl*cyclo*telluropentane*-3 : 5-*dione* (I), which also manifests its diketonic structure by forming a *dioxime* (II).



Hitherto the *cyclo*telluripentanedione dichlorides have been obtained only from exclusively aliphatic β-diketones, but this condensation has now been brought about both with 3-*benzylacetylacetone* and with 3 : 3-*dibenzylacetylacetone*. The two resulting *telluridichlorides* show the characteristic cyclic property of reduction to 4-*benzyl*cyclo*telluropentane*-3 : 5-*dione* (III) and 4 : 4-*dibenzyl*-cyclo*telluropentane*-3 : 5-*dione* (IV), the formation of the latter substance being of special interest in confirming the observation, already made with 3 : 3-dialkylacetylacetones, that a β-diketone still furnishes a chelate group to tellurium even when both the hydrogen atoms of the methylene group have been replaced by hydrocarbon radicals.

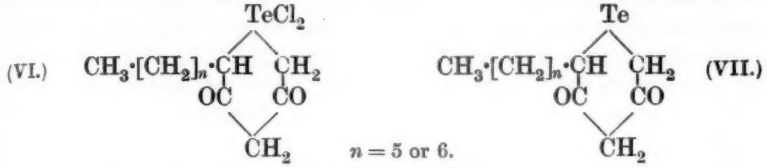
The diketonic constitution of the monobenzyl compound (III) is confirmed by the formation of its *dioxime*.

In a previous communication on tellurium derivatives of diketones (J., 1924, **125**, 731), it was shown that one terminal branched chain inhibited the formation of cyclic derivatives containing $TeCl_2$ linked with a bivalent chelate group.

The simplest case of a β-diketone with branched chains at both ends has now been investigated by attempting to condense tellurium tetrachloride with *di*isobutyrylmethane. This new diketone interacted with very great difficulty, nine-tenths of the combined tellurium was eliminated in the elemental condition, and only a very small amount of telluriferous product was obtained which had the reactions of *tellurium* O-*ethyldi*isobutyrylmethane *trichloride*, $(CH_3)_2CH\cdot C(O\cdot C_2H_5):CH\cdot CO\cdot C(CH_3)_2\cdot TeCl_3$ (V). This evidence and the following data show very plainly that branching of the hydrocarbon chain rather than its length is the inhibiting factor in the production of *cyclo*telluripentanedione dichlorides.

When β-diketones containing comparatively long normal (un-

branched) chains are condensed with tellurium tetrachloride, cyclic dichlorides are obtained.



The condensation was tested on n-*octoylacetone*,

$$C_7H_{15}\cdot CO\cdot CH_2\cdot CO\cdot CH_3,$$

and n-*nonoylacetone*, $C_8H_{17}\cdot CO\cdot CH_2\cdot CO\cdot CH_3$. The isolation of the dichlorides became increasingly difficult because of their greater solubility and fusibility as the series is ascended.

The reaction between *n*-nonoylacetone and tellurium tetrachloride not only furnished the cyclic dichloride (VI), but gave also a considerable proportion of *tellurium* n-*nonoylacetone trichloride*, $CH_3\cdot[CH_2]_6\cdot CH_2\cdot CO\cdot CH{:}C(OH)\cdot CH_2\cdot TeCl_3$, this being the third case observed of the formation of an enolisable trichlorotellurium derivative, the other two analogous products being derived from *n*-heptoylacetone and dibutyrylmethane (J., 1924, **125**, 738, 757).

Experimental.

2 : 6-*Dimethyl*cyclo*telluropentane*-3 : 5-*dionedioxime* (II, R=H).—When condensed with tellurium tetrachloride, dipropionylmethane yielded 2 : 6-dimethyl*cyclo*telluropentane-3 : 5-dione 1 : 1-dichloride together with tellurium *O*-ethyldipropionylmethane trichloride as by-product. The former when reduced with bisulphite furnished 2 : 6-dimethyl*cyclo*telluropentane-3 : 5-dione, which was warmed for 10 minutes with excess of partially neutralised hydroxylamine sulphate in aquo-alcoholic solution. The separated dioxime crystallised from hot dilute alcohol in pale yellow needles decomposing at 168—170° : 0·1490 gave 13·6 c.c. of N_2* at 21° and 743 mm., N = 10·15. $C_7H_{12}O_2N_2Te$ requires N = 9·88%. This dioxime is insoluble in water, although dissolving freely in aqueous caustic soda.

2 : 4 : 6-*Trimethyl*cyclo*telluropentane*-3 : 5-*dione*.

3-*Methyldipropionylmethane*, $CH_3\cdot CH(CO\cdot C_2H_5)_2$.—Sodium dipropionylmethane was heated under reflux with excess of methyl iodide, and the 3-alkyl-diketone isolated as in a similar experiment (J., 1924, **125**, 748). 3-Methyldipropionylmethane was a colourless, mobile liquid, b. p. 92°/10 mm. (yield 10 g. from 12·8 g. of

* In this and the following nitrogen estimations the gas was moist.

dipropionylmethane). It was miscible with the ordinary organic solvents; its alcoholic solution developed a deep violet coloration with ferric chloride. The *copper* salt, obtained by the action of ammoniacal cupric acetate, crystallised from benzene in silky, grey tufts decomposing at 172—173°; it dissolved in hot petroleum (b. p. 40—60°) to an olive-green solution which, on cooling, deposited a woolly mass of grey needles: 0·4288 gave 0·0988 CuO, Cu = 18·60. $C_{16}H_{26}O_4Cu$ requires Cu = 18·36%.

When dissolved in boiling methyl or ethyl alcohol, a light blue copper salt was formed, a colour change indicating the formation of a mixed alkyloxy-copper compound, Et·CO·CMe·CEt·O·Cu·OAlk (*loc. cit.*, p. 746). Ten g. of 3-methyldipropionylmethane were heated for 2½ hours on the water-bath with 70 c.c. of purified chloroform and 9·5 g. of tellurium tetrachloride; the clear liquid was then concentrated in a vacuum desiccator, and in a few days the viscid residue yielded several crops of crystals which on recrystallisation from warm acetone were obtained in colourless needles darkening at 180°. The yield was 68% and no other telluriferous product was obtained: 0·2102 gave 0·1766 AgCl, Cl = 20·80. $C_8H_{12}O_2Cl_2Te$ requires Cl = 20·96%.

2 : 4 : 6-*Trimethyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*dichloride* was sparingly soluble in the ordinary organic media with the exception of acetone. With aqueous potassium metabisulphite (2 mols.) in the cold, the dichloride was reduced almost quantitatively to 2 : 4 : 6-*trimethyl*cyclo*telluropentane*-3 : 5-*dione* (I, R = CH_3), which was slightly soluble in cold water to a yellow neutral solution having powerful bactericidal properties but much less active in this respect than the solution of 2 : 6-dimethyl*cyclo*telluropentane-3 : 5-dione. The new trimethylated compound crystallised from alcohol in bright yellow needles darkening at 133° and melting with decomposition at 135°: 0·1640 gave 0·2152 CO_2 and 0·0677 H_2O, C = 35·79, H = 4·58; 0·2355 gave 0·1130 Te, Te = 47·90. $C_8H_{12}O_2Te$ requires C = 35·89, H = 4·48, Te = 47·66%.

2 : 4 : 6-*Trimethyl*cyclo*telluropentane*-3 : 5-*dionedioxime* (II, R = CH_3), prepared as in the experiment on p. 799, separated from the cooled solution in yellowish-green plates which, after extraction with hot benzene, were recrystallised from acetylacetone and separated in yellow flakes decomposing at 170°: 0·1700 gave 13·8 c.c. N_2 at 22° and 748·5 mm., N = 9·1. $C_8H_{14}O_2N_2Te$ requires N = 9·41%.

4-*Benzyl*cyclo*telluropentane*-3 : 5-*dione* (III).

Purified acetylacetone was added to the calculated quantity of sodium dissolved in absolute alcohol, when sodium acetylacetone separated in masses of glistening needles, which were dried at 60°

on porous plates. This sodium derivative (50 g.) mixed with 150 g. of benzyl chloride was heated at 160—200° for 8 hours; the reaction commenced at 120°. The filtrate from sodium chloride was distilled up to 260° to remove excess of benzyl chloride; the residue was then fractionated under reduced pressure, when 30 g. of 3-*benzylacetylacetone* were obtained as a colourless oil, b. p. 150°/3 mm. (yield 39%). The viscid, black, oily residue yielded subsequently 3 : 3-*dibenzylacetylacetone* (see p. 802).

3-*Benzylacetylacetone*, $C_6H_5 \cdot CH_2 \cdot CH(CO \cdot CH_3)_2$, a mobile liquid with a sharp odour, was readily miscible with petroleum, benzene, or chloroform, but not with water; its alcoholic solution gave an intense violet coloration with ferric chloride, and with ammoniacal cupric acetate it furnished the *copper* salt as a light grey precipitate, which on repeated crystallisation from benzene separated in grey needles, m. p. 176°: 0·5030 gave 0·0886 CuO, Cu = 14·1. $C_{24}H_{26}O_4Cu$ requires Cu = 14·37%. *Copper* 3-*benzylacetylacetone* was sparingly soluble in cold organic solvents, but dissolved in hot alcohol or benzene to green solutions from which it separated in neutral grey needles.

4-*Benzyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*Dichloride*.—3-Benzylacetylacetone (5·8 g.) and 2·7 g. of tellurium tetrachloride dissolved in 20 c.c. of boiling chloroform to a yellowish-red solution which darkened and evolved hydrogen chloride. After removing 0·3 g. of tellurium, the solution was concentrated under reduced pressure to a viscid glue. A portion washed with carbon tetrachloride and extracted with chloroform furnished, on evaporating off the solvent, a few white crystals, which were utilised in inoculating the main batch, about 2 g. of telluridichloride being thus obtained. The product crystallised from benzene on addition of light petroleum in white flakes decomposing at 180°: 0·2054 gave 0·1520 AgCl, Cl = 18·31. $C_{12}H_{12}O_2Cl_2Te$ requires Cl = 18·37%.

The foregoing dichloride was reduced smoothly with aqueous metabisulphite, the precipitate being crystallised by concentrating its cold benzene solution.

4-*Benzyl*cyclo*telluropentane*-3 : 5-*dione* (III) dissolved sparingly in boiling water and readily in hot organic media, separating from alcohol in light yellow, glistening flakes; from acetylacetone solutions large, prismatic crystals were obtained, m. p. 153° (decomp.): 0·1506 gave 0·2524 CO_2 and 0·0540 H_2O, C = 45·71, H = 3·98; 0·2517 gave 0·1020 Te, Te = 40·43. $C_{12}H_{12}O_2Te$ requires C = 45·64, H = 3·81, Te = 40·41%.

4-*Benzyl*cyclo*telluropentane*-3 : 5-*dionedioxime*, prepared as on p. 799, was precipitated as a flocculent, yellow-green mass sparingly soluble in hot benzene and separating therefrom as a yellowish-

green powder, decomposing at 168—170°: 0·1606 gave 11·75 c.c. N_2 at 18° and 735 mm., N = 8·15. $C_{12}H_{14}O_2N_2Te$ requires N = 8·10%.

Insoluble in water, the oxime dissolved in cold aqueous caustic soda to a yellow solution which deposited tellurium on boiling.

4 : 4-*Dibenzyl*cyclo*telluropentane*-3 : 5-*dione* (IV).

3 : 3-*Dibenzylacetylacetone*, $(C_6H_5\cdot CH_2)_2C(CO\cdot CH_3)_2$, was obtained as a by-product in the preparation of 3-benzylacetylacetone. The dark oily residue left after distilling off the monobenzyl compound was fractionated further and at 200—227°/3 mm. a distillate was obtained which solidified to a mass of acicular crystals coloured yellow by impurities, which were removed with cold ether. After two crystallisations from alcohol, it melted at 111—112° (yield 2 g. or 1·5%): 0·0998 gave 0·2970 CO_2 and 0·0646 H_2O, C = 81·2, H = 7·19. $C_{19}H_{20}O_2$ requires C = 81·43, H = 7·14%.

This β-diketone was insoluble in water and dissolved only sparingly in cold organic solvents. It separated from ether in transparent, colourless prisms, developed no coloration with ferric chloride, and did not furnish a copper salt with ammoniacal cupric acetate. It did not condense with *p*-nitrophenylhydrazine.

3 : 3-*Dibenzylacetylacetone from* 3-*Benzylacetylacetone*.—Sodium (1·6 g.), cut into thin slices, was added to 3-benzylacetylacetone (12·8 g.) dissolved in 100 c.c. of dry ether. After the metal had dissolved completely, the solution became semi-solid owing to the separation of *sodium* 3-*benzylacetylacetone*, a voluminous, white powder, m. p. 109°, and soluble in cold alcohol or water, reacting with cupric acetate to yield a grey copper derivative. The dry sodium derivative (25 g.) was heated with 70 g. of benzyl chloride at 200—210° for 11 hours. The precipitated sodium chloride was washed with ether. The ethereal filtrate was evaporated and distilled under reduced pressure to eliminate excess of benzyl chloride. The oily residue, inoculated with a crystal of 3 : 3-dibenzylacetylacetone, solidified to a light brown mass. When purified by crystallisation from alcohol, 10 g. of the dibenzyl compound were obtained (yield 30%).

4 : 4-*Dibenzyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*dichloride* was produced by condensing 3·3 g. of dibenzylacetylacetone with 2·6 g. of tellurium tetrachloride in 30 c.c. of pure chloroform. After 2—3 hours, the solution had darkened considerably and tellurium was deposited. The filtrate, concentrated to a small bulk, was extracted with petroleum (b. p. 40—60°) to remove unchanged β-diketone, and the oily residue left to crystallise in a vacuum desiccator. After 1 month, the solid product was washed

with cold benzene, and the insoluble residue crystallised from chloroform, preferably with the addition of light petroleum; white flakes were obtained, m. p. 189—190° (decomp.) (yield 1 g. or 23%): 0·2048 gave 0·1268 AgCl, Cl = 15·3. $C_{19}H_{18}O_2TeCl_2$ requires Cl = 14·9%).

This dichloride dissolved sparingly in cold organic solvents excepting acetone, in which it was moderately soluble.

Reduction with aqueous metabisulphite occurred very slowly owing to the sparing solubility of the dichloride. After 6 hours, a bright yellow powder remained, which on repeated crystallisation from dilute alcohol formed yellow needles softening at 123° and melting at 128°: 0·0961 gave 0·1976 CO_2 and 0·0390 H_2O, C = 56·08, H = 4·51. $C_{19}H_{18}O_2Te$ requires C = 56·23, H = 4·44%.

4 : 4-*Dibenzyl*cyclo*tellluropentane*-3 : 5-*dione* (IV) dissolved in benzene, but not in water or aqueous caustic alkalis, thus showing no residual acidity; it was quite stable to the boiling alkali.

Tellurium tetrachloride did not condense in chloroform with 3 : 3-di-*p*-nitrobenzylacetylacetone (Mech, *Compt. rend.*, 1906, **143**, 753; 1908, **146**, 1410), and it was not found possible by varying the experimental conditions to prepare 3-*p*-nitrobenzylacetylacetone. Sodium acetylacetone did not interact with *p*-nitrochlorobenzene after prolonged boiling in alcoholic solution.

*Di*isobutyrylmethane, $CH_2[CO{\cdot}CH(CH_3)_2]_2$.

Although both di-*n*-butyrylmethane and *n*-butyryl*iso*butyrylmethane are known, the di*iso*-compound has not hitherto been described. It was prepared through its highly characteristic copper salt as follows: A mixture of 20 g. of methyl *iso*propyl ketone, 80 g. of ethyl *iso*butyrate, and 5·7 g. of sodium was kept at 0° for several hours, then allowed to attain the laboratory temperature. After 2 days, the mixture was poured on to crushed ice, the aqueous layer separated quickly, washed with ether, acidified, and treated with cupric acetate, when a bluish-green precipitate was obtained.

The ester layer was shaken with a large bulk of water, the aqueous portion separated, washed with ether, and run into aqueous cupric acetate containing acetic acid, when dark blue copper di*iso*butyrylmethane separated (5·6 g.). The foregoing bluish-green precipitate was extracted with petroleum (b. p. 40—60°), when green copper *iso*butyrate remained undissolved whilst the petroleum extract yielded another crop of the dark blue copper diketone.

When crystallised repeatedly from petroleum (b. p. 40—60°), *copper di*iso*butyrylmethane* was obtained in large, intensely blue rhombohedra; each crystal was a perfect parallelepiped showing

no facets, m. p. 113—114° : 0·6740 gave 0·1432 CuO, Cu = 16·79; 0·1154 gave 0·2442 CO_2 and 0·0850 H_2O, C = 57·7, H = 8·19. $C_{18}H_{30}O_4Cu$ requires Cu = 17·02, C = 57·83, H = 8·03%.

This copper salt was very soluble in cold organic solvents, giving bluish-green solutions. In hot benzene, it dissolved so readily that even in thin layers the liquid was opaque. The free ketone, isolated from its copper derivative (15 g.) by dilute sulphuric acid in presence of ether, was obtained from the ethereal extract as a colourless, mobile liquid, b. p. 75—77°/7 mm. (yield 10 g.). It was miscible with organic media and its alcoholic solution developed a bright red ferric coloration.

Diisobutyrylmethane and Tellurium Tetrachloride.—A yellow solution resulted on mixing 6 g. of the diketone, 5·5 g. of tellurium tetrachloride, and 30 c.c. of chloroform, and on heating under reflux the colour changed through red to black; a considerable amount of hydrogen chloride was evolved and tellurium (1·9 g.) was deposited. After 2 hours, the light brown filtrate was concentrated in a vacuum desiccator, more tellurium being deposited (0·3 g.); the oily residue was extracted with light petroleum, and the yellow solution deposited hard, colourless, compact, tabular crystals (0·03 g.), m. p. 87—89° (decomp.), and left a residue of unchanged diketone. Qualitative analysis showed the presence of tellurium and chloride. The compound was not reducible to a yellow telluro-derivative, hence was not a *cyclo*telluripentanedione dichloride; it developed no ferric chloride coloration and was accordingly neither a telluritrichloro-derivative,

$$(CH_3)_2CH\cdot C(OH){:}CH\cdot CO\cdot C(CH_3)_2\cdot TeCl_3,$$

nor a telluridichloro-compound,

$$\{(CH_3)_2\cdot CH\cdot CO\cdot CH{:}C(OH)\cdot C(CH_3)_2\}_2TeCl_2.$$

On decomposition with aqueous alkali the compound developed the earthy odour characteristic of *O*-ethyl β-diketones. Hence by exclusion the product of the condensation was probably *tellurium O-ethyldiisobutyrylmethane trichloride* (V). But owing to the very small yield the further study of the compound was not pursued.

Higher n-*Acylacetones and Tellurium Tetrachloride.*

For the two higher β-diketones employed in this section we are indebted to Mr. E. Holmes (*J. Soc. Chem. Ind.*, 1925, **44**, 108T).

1. *n*-Octoylacetone, a colourless, mobile liquid with the odour characteristic of β-diketones, boiled at 249°/755 mm. or at 117—118°/5 mm.

2-n-*Hexyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*Dichloride* (VI).—The orange-red solution of 8 g. of *n*-octoylacetone and 5·9 g. of tellurium tetrachloride in 20 c.c. of dry chloroform soon blackened on heating,

but only 0·3 g. of tellurium was deposited in 4 hours. The dark brown filtrate was concentrated at the ordinary temperature and freed from unchanged diketone by repeated extraction with light petroleum, the residue concentrated further, and cooled in the ice chest. After 3 weeks, crystallisation set in. The product (1·5 g.) was stirred with carbon tetrachloride and washed with light petroleum. The carbon tetrachloride extract gave a further 0·5 g. of the dichloride (total yield 25%). The crude material was dissolved in warm benzene, filtered from tellurium, and the filtrate diluted with *n*-hexane, when colourless, glistening flakes separated, m. p. 80°: 0·1577 gave 0·1194 AgCl, Cl = 18·70. $C_{11}H_{18}O_2Cl_2Te$ requires Cl = 18·66%.

The dichloride was readily soluble in alcohol, chloroform, or benzene, less soluble in carbon tetrachloride, and sparingly soluble in petroleum or water.

2-n-*Hexyl*cyclo*telluropentane*-3 : 5-*dione* (VII), produced by reduction of the preceding dichloride with cold aqueous potassium metabisulphite, was crystallised from dilute alcohol and separated in bright yellow scales, m. p. 74—75°. It dissolved readily in organic solvents, but only sparingly in water. It possessed residual acidity, dissolving in cold aqueous caustic soda, but gave no ferric coloration: 0·0969 gave 0·1510 CO_2 and 0·0540 H_2O, C = 42·50, H = 6·10; 0·2060 gave 0·0836 Te, Te = 40·59. $C_{11}H_{18}O_2Te$ requires C = 42·65, H = 5·84, Te = 41·19%.

2. *n*-Nonoylacetone, liberated from its copper salt, was a colourless, mobile liquid boiling at 140°/3 mm. On cooling in ice, it solidified to a crystalline mass, m. p. 24°, miscible with ordinary organic solvents including petroleum.

2-n-*Heptyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*Dichloride* (VI).—The yellow mixture of 9 g. of *n*-nonoylacetone, 8 g. of tellurium tetrachloride, and 30 c.c. of pure dry chloroform was heated for 3 hours, filtered from 0·4 g. of tellurium, and concentrated in a vacuum desiccator. After several days, crystallisation began and 3 g. of grey product were obtained. Purified by adding petroleum (b. p. 40—60°) to its chloroform solution, the dichloride separated in colourless plates, m. p. 89°: 0·2020 gave 0·1458 AgCl, Cl = 17·85; $C_{12}H_{20}O_2Cl_2Te$ requires Cl = 17·98%.

2-n-*Heptyl*cyclo*telluropentane*-3 : 5-*dione* (VII), prepared by the bisulphite reduction of the foregoing dichloride, separated from hot dilute alcohol in bright yellow, woolly masses, m. p. 89°: 0·1105 gave 0·1829 CO_2 and 0·0638 H_2O, C = 45·14, H = 6·61; 0·2620 gave 0·1020 Te, Te = 38·94. $C_{12}H_{20}O_2Te$ requires C = 44·52, H = 6·18, Te = 39·41%.

This telluro-derivative was only sparingly soluble in water, but

exhibited residual acidity by dissolving more readily in dilute aqueous caustic soda to a solution depositing tellurium on boiling.

Tellurium n-*Nonoylacetone Trichloride.*—Tellurium tetrachloride (4 g.) was mixed with 4·5 g. of nonoylacetone in chloroform solution and refluxed for 2½ hours. After concentrating the clear solution in a vacuum desiccator for 48 hours, the solid which separated was freed from tarry matter by washing successively with carbon tetrachloride and petroleum (b. p. 40—69°) and crystallised by dissolving in warm chloroform with the addition of light petroleum, when colourless, glistening flakes were obtained, m. p. 114—115° with blackening (yield 1 g.). Its chloroform–alcohol solution instantly developed a ferric coloration: 0·1557 gave 0·1555 AgCl, Cl = 24·70. $C_{12}H_{21}O_2Cl_3Te$ requires Cl = 24·71%.

Tellurium *n*-nonoylacetone trichloride was slowly decomposed by moisture, liberating the diketone and depositing tellurium dioxide; its ether–chloroform solution gave with aqueous cupric acetate a pale green precipitate of a copper salt. When boiled with chloroform, it did not evolve hydrogen chloride, but was decomposed on treatment with aqueous metabisulphite.

From the mother-liquors of the foregoing trichloride 0·5 g. of the cyclic dichloride was subsequently isolated.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research and to the Government Grant Committee of the Royal Society for grants which have helped to defray the expense of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, January 30th,* 1925.]

CXIV.—*The Interaction of Hydrogen and Carbon Dioxide on the Surface of Platinum.*

By CHARLES ROSS PRICHARD and CYRIL NORMAN HINSHELWOOD.

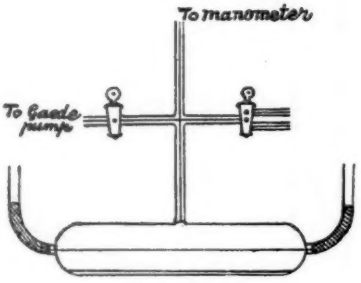
HYDROGEN and carbon monoxide are known to form adsorbed layers on the surface of platinum which are stable at quite high temperatures, and which largely determine the mechanism of catalytic reactions undergone by these gases in contact with the metal. Little is known about the adsorption of carbon dioxide. The kinetics of the reaction $H_2 + CO_2 = H_2O + CO$ on the surface of a heated platinum wire present points of interest in connexion with the relative adsorptions of the various gases. The interaction of carbon dioxide and hydrogen has been investigated from 870° to 1122°, over which range the change proceeds at a con-

veniently measurable rate. It was made irreversible by the absorption of the water formed, and was shown to go to completion, analysis proving the product to consist entirely of carbon monoxide. No hydrocarbons are formed under these conditions.

The apparatus consisted of a cylindrical bulb with an axial electrically heated platinum wire, the temperature of which was known from its resistance, and could be controlled so that reaction velocities were reproducible to 1%. The bottom of the vessel contained concentrated sulphuric acid to absorb water, and the apparatus was kept in ice during the experiments. The rate of reaction was found by changes in pressure exactly as described for the catalytic decomposition of nitrous oxide (this vol., p. 327). The actual reaction bulb is shown in Fig. 1.

The continuous and accurate control of the energy supplied to the wire was even more important than in the nitrous oxide experiments owing to the rapidly changing thermal conductivity of the gas mixture. It presented no difficulty, however. Provided that the wire was heated to 1000° in a high vacuum between the experiments, satisfactorily reproducible results were obtained. The hydrogen was electrolytic, passed over heated platinum to remove oxygen; carbon dioxide was obtained from magnesite. Both gases were dried with phosphorus pentoxide. Nearly 200 separate fillings were made. In many cases complete reaction–time curves were plotted, but always the amount of change after at least two fixed periods of time was noted.

Fig. 1.



Most of the experiments were made at 1000°. The results were as follows. Each statement is based upon several complete series of experiments.

1. When the pressure of carbon dioxide is kept constant, the rate of formation of carbon monoxide increases almost linearly with the pressure of hydrogen, at least up to 300 mm. This is shown in curves I and II of Fig. 2.

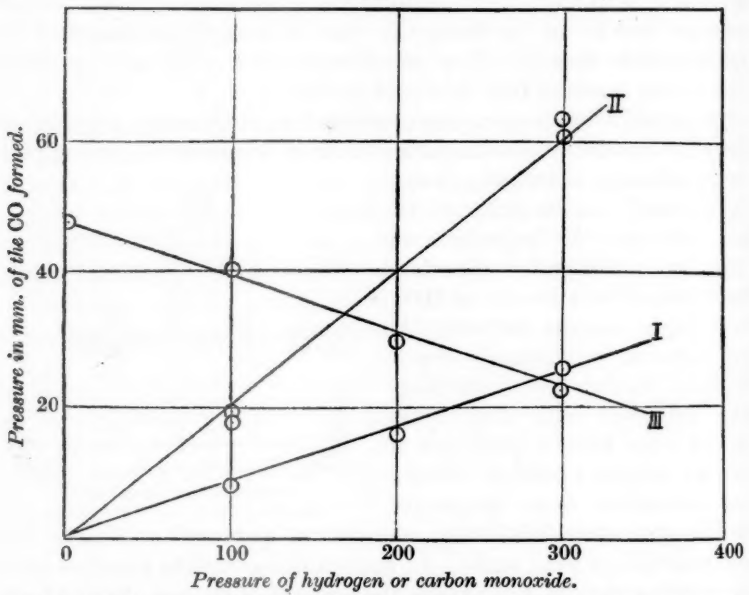
2. When the pressure of hydrogen is kept constant, the rate of reaction is at first proportional to the pressure of carbon dioxide, and then passes through a maximum when the pressure of carbon dioxide is about double that of the hydrogen. Larger pressures of carbon dioxide have a great retarding influence, although it is remarkable that the sharpness of the maximum seems to vary

with the state of the wire. These points are illustrated by the curves in Fig. 3.

3. Carbon monoxide has a slight retarding influence, but considerably less than might have been expected (curve III, Fig. 2).

4. When the reacting gases are in equimolecular proportions (the pressure of each being 100 mm.), the course of the reaction is very nearly unimolecular, the time required for three-quarters of the reaction to complete itself being double that for half. But

FIG. 2.



I 870°; 100 *mm. carbon dioxide in each instance. Abscissæ represent varying* H_2 *pressures, ordinates give the pressure in mm. of the* CO *formed in* 1,200 *seconds;* II 1000°, 300 *seconds, otherwise as* I. III 100 *mm.* H_2; 100 *mm.* CO_2. *Abscissæ show pressure of added* CO; *ordinates, the reaction in* 300 *seconds.* 1000°.

the previous results show that this is to some extent a coincidence. A typical experiment illustrating the course of the reaction is given below, t being the time in seconds and x being the pressure in mm. of the carbon monoxide formed.

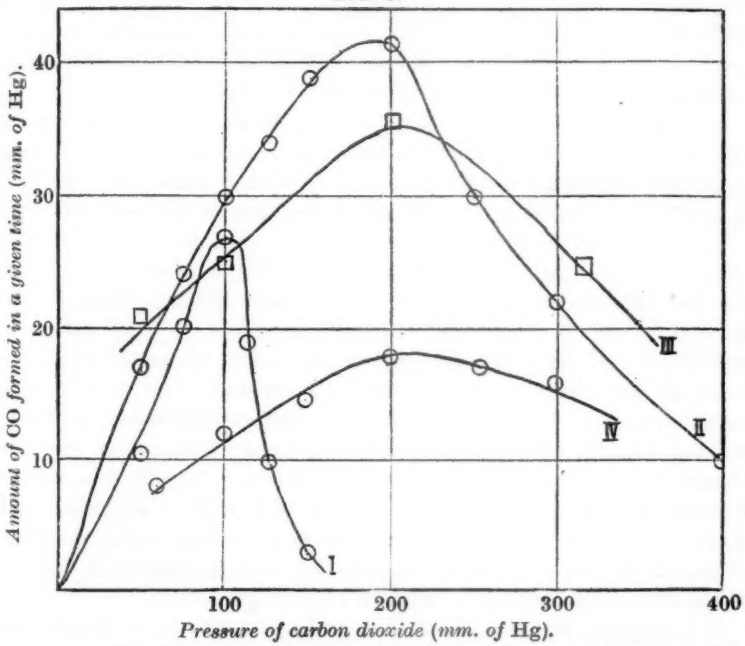
Temp. 1050°; pressure of H_2 = 100 mm.; pressure of CO_2 = 100 mm.

t	120	300	400	600	800	1000	1200	1400	1800	∞
x	16	30	37·5	51	61	68·5	75	79·5	85	99

The influence of the pressures of the various gases is shown in the curves. The employment of the amount of change in 120

or 300 seconds as a measure of the rate of reaction is justified by the small deviation only of the reaction–time curves from linearity in their initial stages. Other methods of presenting the results give curves exactly like those in the figures. To ensure that the results were not influenced by any drift in catalytic activity, the experiments of a given series were made in a random order, and after each two or three a control experiment was made at some standard pressure to ascertain that the wire had not changed.

FIG. 3.



I 50 *mm.* H_2; 1000°; 300 *seconds.* II 100 *mm.* H_2; 1000°; 300 *seconds.* III 100 *mm.* H_2; 1120°; 120 *seconds.* IV 100 *mm.* H_2; 1000°; 120 *seconds* *State of wire different in* II *and* IV.

For example, in the series shown in Fig. 3, curve II, two experiments with carbon dioxide and hydrogen each at 100 mm. pressure showed the percentage formation of carbon monoxide to be 17 and 17·5 after 120 seconds and 30 and 30 after 300 seconds, six experiments intervening.

Since the rate of reaction is dependent on the adsorption of three different gases, the influence of temperature is so complex as to be of little interest at present. An empirical temperature coefficient was, however, determined. For 100 mm. of hydrogen and 100 mm. of carbon dioxide the initial rate of reaction increases

2·85 times for 100° over the range 900° to 1100°. This gives an apparent heat of activation of approximately 33,000 calories.

Perhaps the most remarkable result is the apparent strong adsorption of carbon dioxide shown by its poisoning effect at higher pressures. At lower temperatures carbon dioxide is not much adsorbed by platinum, and experiments specially made on the relative adsorption of hydrogen and carbon dioxide by platinised asbestos at 970° showed strong adsorption of hydrogen, that of carbon dioxide being negligible in comparison, and indeed indistinguishable from the adsorption, if any, of the nitrogen used for calibrating the apparatus. We must therefore assume that the catalytic activity of the surface is localised in certain active points forming a small fraction only of the total surface.

A simple mechanism which now accounts for most of the facts is that reaction occurs when hydrogen and carbon dioxide become adsorbed adjacent to each other on an active part of the surface. It must be assumed further that the fraction of the active surface covered by carbon dioxide increases from zero to nearly unity as the pressure of carbon dioxide increases from 0 to 400 mm., whilst the adsorption of hydrogen on those points left free from carbon dioxide is never very great, so that we have to deal with that portion of the hydrogen adsorption isotherm where adsorption is more or less directly proportional to pressure. (It is true that saturation, although not reached in the experiments, would be reached at pressures considerably higher than 300 mm.) We then obtain the equation $d[\mathrm{CO}]/dt = k[\mathrm{H_2}]\sigma(1 - \sigma)$, where σ is the fraction of the active surface covered with carbon dioxide. This gives the linear dependence on hydrogen pressure over the range of pressures used in the experiments, and the maximum in the rate of reaction with increase of carbon dioxide pressure.

It is remarkable that there does not appear to be a simple competition between the hydrogen and carbon dioxide for the active surface, the hydrogen occupying all the active points left unoccupied by carbon dioxide. If this were so, the velocity would not vary linearly with the hydrogen pressure over so large a range, and the hydrogen curves would resemble the carbon dioxide curves. The results throw an interesting light on the adsorptive capacity of the surface, since it appears that the relative adsorbability of hydrogen and carbon dioxide on the active points bears no relation to that on the total surface. Moreover, unpublished experiments of Burk and Hinshelwood have shown that even at these high temperatures the decomposition of ammonia on platinum is retarded by hydrogen in a way which shows that even at 100 mm. the hydrogen covers quite a large fraction of the surface which

is active in causing the decomposition of ammonia. We have also found that carbon dioxide at a pressure of 400 mm. has only a slight retarding effect on the decomposition of nitrous oxide on platinum—the same wire as that used in the present series of experiments—confirming the conclusion that the points on which the carbon dioxide is adsorbed constitute only a small fraction of the surface.

We are indebted to the Royal Society and to the Chemical Society for grants in aid of this work.

PHYSICAL CHEMISTRY LABORATORY,
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OXFORD. [*Received, January 24th*, 1925.]

CXV.—*Asymmetric Compounds of Quinquevalent Arsenic.*

By JOHN ALFRED AESCHLIMANN.

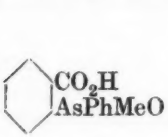
ATTEMPTS to resolve quaternary arsonium compounds by means of camphor- or bromocamphor-sulphonic acid have been made by Michaelis (*Annalen*, 1902, **321**, 158), Winmill (J., 1912, **101**, 720), and Burrows and Turner (J., 1921, **119**, 426), but in no case were two forms of the salt isolated.

Compounds of the type abcAs:O have now been investigated in which one of the groups a, b, and c contains an acidic radical for combination with an active base in order to effect the resolution. It was hoped that the removal of the active group would have less tendency to alter the spatial arrangement of the groups round the central atom than is the case when the active group is attached to the arsenic atom as in the older method (compare Kipping, J., 1910, **97**, 755; Jones, *Proc. Camb. Phil. Soc.*, 1904, **12**, 489; Meisenheimer, *Ber.*, 1924, **57**, 1744); and that racemisation might thus be prevented.

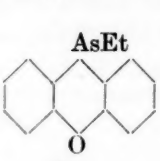
No evidence of resolution was obtained, however, in the case of *oo'*-dicarboxydiphenylarsinic anhydride (Aeschlimann and McCleland, J., 1924, **125**, 2025), or o-*carboxydiphenylmethylarsine oxide* (I). Phenyl-α-naphthylmethylarsine oxide, the resolution of which was attempted by Burrows and Turner (*loc. cit.*), yielded a crystalline sulphonic acid on sulphonation. The brucine and quinine salts of the acid were amorphous and the various fractions into which the crystalline strychnine salt was separated all gave rise to an inactive ammonium salt. *l*-Phenylethylamine also failed to effect resolution.

o-*Carboxydiphenylmethylarsine*, the production of which from

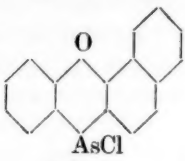
o-carboxyphenylmethylchloroarsine and benzene by the Friedel-Crafts reaction is unsatisfactory (compare Burrows and Turner, *loc. cit.*, p. 430), is readily obtained by the interaction of magnesium phenyl bromide and *o*-carboxyphenylmethylarsinous anhydride (Aeschlimann and McCleland, *loc. cit.*, p. 2033). This reaction may prove to be of value for the preparation of arsines containing a carboxyl group, the only method hitherto available being the oxidation of tolylarsines (Michaelis, *loc. cit.*) and reduction of the oxide produced.



(I.)



(II.)



(III.)

10-Ethylphenoxarsine (II), which has been obtained as a colourless oil (contrast Lewis, Lowry, and Bergheim, *J. Amer. Chem. Soc.*, 1921, **43**, 891, where a compound, m. p. 218°, is named 6-ethylphenoxarsine), combines readily with alkyl iodides and with bromoacetic acid to form stable, crystalline, quaternary salts which it is hoped to examine further. The addition compound with bromoacetic acid produces brucine hydrobromide when it is treated with brucine, as does also carboxymethylphenyl-α-naphthylmethylarsonium bromide, and the resulting glassy betaine does not combine further with brucine.

10-Ethylphenoxarsine can be oxidised to a water-soluble arsine oxide, which forms a hydrate. Either the arsine or its oxide can be sulphonated and the sulphonic acid produced gives alkaloid salts which are very soluble in water.

Phenyl α-naphthyl ether condenses with arsenious chloride in presence of aluminium chloride to produce *7-chloro-αβ-naphthaphenoxarsine* (III).

Experimental.

oo'-Dicarboxydiphenylarsinic anhydride (Aeschlimann and McCleland, *loc. cit.*), crystallised from hot water, was kept over sulphuric acid for 4 weeks, until its weight had become constant (Found: loss = 5·2. $C_{14}H_9O_5As,H_2O$ requires $H_2O = 5{\cdot}1\%$). The anhydride ring, therefore, is not very stable.

The hygroscopic quinine salt, the brucine salt, and the phenylethylamine salt each gave an inactive acid after removal of the base.

o-*Carboxydiphenylmethylarsine.*—Magnesium phenyl bromide (prepared from 30 g. of bromobenzene in ether) was added to 42 g. of *o*-carboxyphenylmethylarsinous anhydride in benzene during 30 minutes, and the mixture heated for 4 hours. After removal

of the solvent, the residue was treated with dilute acid, the aqueous layer removed, and the pasty residue crystallised from alcohol (yield 20 g.); m. p. 168°. Unchanged anhydride was recovered from the mother-liquor (Found: C = 57·8; H = 4·5; As, by direct titration with iodine, = 26·7. $C_{14}H_{13}O_2As$ requires C = 58·3; H = 4·5; As = 26·1%).

o-*Carboxydiphenylmethylarsine Oxide* (I).—The preceding arsine in warm alcoholic solution was oxidised with hydrogen peroxide. The product crystallised from alcohol or acetic acid in colourless needles, m. p. 242° (Found: C = 55·4; H = 4·3. $C_{14}H_{13}O_3As$ requires C = 55·3; H = 4·3%). If the crude arsine is used for the preparation of the oxide, *o*-carboxyphenylmethylarsinic acid remains in the aqueous alcoholic solution.

Alkaloid salts were obtained neither from the acid (I) in alcoholic solution nor from its sodium salt and alkaloid hydrochloride. The *l*-phenylethylamine salt, obtained by using an excess of the base in aqueous solution, appeared to decompose on heating with water. It was separated into three fractions by crystallisation from warm water, but the arsine oxide recovered from them was inactive.

The brucine salt (5 g.) of *o*-carboxydiphenylmethylarsine, on oxidation with hydrogen peroxide, gave 2·2 g. of the preceding arsine oxide, complete decomposition of the salt therefore having taken place.

Sulphophenyl-α-naphthylmethylarsine Oxide.—A solution of 10 g. of phenyl-α-naphthylmethylarsine oxide (prepared by oxidising the arsine [Burrows and Turner, *loc. cit.*] with hydrogen peroxide in acetone or alcohol and recrystallising the product from toluene) in 20 c.c. of oleum (20% SO_3) was allowed to cool and poured into water. The precipitate was dissolved in aqueous ammonia, and the solution boiled with charcoal and filtered into hot acetic acid, the *sulphonic acid* separating, on cooling, in fine, white crystals, m. p. 249°. Mr. E. S. Dewing, who kindly examined the crystals, reports that they show straight extinction and have a habit similar to that of baryta with two planes of symmetry; the existence of enantiomorphous forms would therefore appear to be impossible (Found: C = 52·1; H = 3·9; S = 8·15. $C_{17}H_{15}O_4SAs$ requires C = 52·4; H = 3·9; S = 8·2%).

The *addition compound* obtained by heating phenyl-α-naphthylmethylarsine and bromoacetic acid on the water-bath for 1 hour crystallised from alcohol to which hydrobromic acid had been added. It melted at 145—150° (decomp.), but was not quite pure (Found: Br = 18·55. $C_{19}H_{17}O_2BrAs$ requires Br = 18·45%).

10-*Ethylphenoxarsine* (II).—A warm solution of 10-chlorophenoxarsine (64 g.) in 200 c.c. of benzene was added to the Grignard re-

agent prepared from 23 c.c. (excess) of ethyl bromide and 7 g. of magnesium. The mixture was heated for 4 hours, decomposed in the usual manner, and the solution dried and distilled in a vacuum; the phenoxarsine (yield 42 g.) passed over at 194°/20 mm., leaving a small quantity of the chlorophenoxarsine. A colourless liquid free from chlorophenoxarsine was obtained by refractionation in a vacuum, but it did not crystallise (Found: C = 61·8; H = 4·8. $C_{14}H_{13}OAs$ requires C = 61·8; H = 4·8%).

10-*Ethylphenoxarsine oxide*, m. p. 99°, was obtained by evaporating a solution of the phenoxarsine in hydrogen peroxide, and crystallised from hot benzene. It contained a molecule of water, which it lost below 60° in a vacuum and regained in the air (Found: C = 54·1; H = 4·9; loss = 5·6%. $C_{14}H_{13}O_2As,H_2O$ requires C = 54·9; H = 4·9; H_2O = 5·8%).

Sulpho-10-*ethylphenoxarsine oxide* was obtained by sulphonating the oxide under similar conditions to those described above, but the mixture was heated at 100°. The acid was soluble in hot water and insoluble in alcohol. It changed in appearance at 250° without charring, but did not melt below 300° (Found: C = 45·4; H = 3·5; equiv. = 368. $C_{14}H_{13}O_5SAs$ requires C = 45·6; H = 3·5%; equiv. = 368).

10-*Methyl*-10-*ethylphenoxarsonium iodide*, formed when equivalent quantities of 10-ethylphenoxarsine and methyl iodide were heated for 4 hours at 50°, crystallised from hot alcohol in compact, white crystals, m. p. 186° or 193° according to the rate of heating (Found: C = 43·1; H = 4·0; I = 30·6. $C_{15}H_{16}OIAs$ requires C = 43·5; H = 3·9; I = 30·7%). An orange-red compound, probably an isomeride, also was obtained.

10-*Methyl*-10-*ethylphenoxarsonium* d-*bromocamphorsulphonate*, m. p. 153°, obtained by treating the white iodide with silver *d*-bromocamphorsulphonate in alcohol, could be crystallised from alcohol or water. Various fractions of the salt had $[M]_{5461}$ + 339° in 1·5% aqueous solution and + 398° in 5% alcoholic solution (compare Winmill, *loc. cit.*) (Found: C = 50·0; H = 5·0. $C_{25}H_{30}O_5BrSAs$ requires C = 50·2; H = 5·0%).

10 : 10-*Diethylphenoxarsonium iodide* crystallises in pale straw-coloured needles, m. p. 193° (Found: C = 45·1; H = 4·3. $C_{16}H_{18}OIAs$ requires C = 44·8; H = 4·2%).

10-*Carboxymethyl*-10-*ethylphenoxarsonium bromide* was obtained by heating 10-ethylphenoxarsine with bromoacetic acid for 10 minutes at 100°, and was sufficiently stable to be recrystallised from hot alcohol (Found: Br = 19·6; equiv. = 412. $C_{16}H_{16}O_3BrAs$ requires Br = 19·5%; equiv. = 411).

7-*Chloro*-αβ-*naphthaphenoxarsine* (III), m. p. 168°, was obtained

by heating a mixture of arsenious chloride, phenyl α-naphthyl ether, and aluminium chloride from 180° to 250°, distilling in a vacuum, and recrystallising from benzene the fraction obtained between 210° and 240°/20 mm. The yield was small and was not improved by various modifications (Found : C = 58·9; H = 2·95. $C_{16}H_{10}OClAs$ requires C = 58·6; H = 3·05%).

Resolution of r-*Phenylethylamine.*—A solution of the base and the equivalent quantity of tartaric acid in boiling alcohol (15 parts) was cooled to 60°, stirred for 24 hours, and the mother-liquor poured off from the heavy, crystalline precipitate of *l*-base *d*-tartrate. The liquor set to a paste of hair-like needles on cooling, but the pure *d*-base could not be obtained from these after repeated crystallisation as described by Betti (*Gazzetta*, 1920, **50**, 276). The impure base liberated from the salt was converted into the *l*-malate in aqueous solution by Loven's method (*J. pr. Chem.*, 1905, **72**, 307), a moderately pure salt of the *d*-base being obtained. The salts of the *d*- and the *l*-base were crystallised once from a little water. The *d*-base *l*-malate gave $\alpha + 0{\cdot}05°$ ($l = 2$) in 5% aqueous solution, whereas a specimen prepared wholly by Loven's method gave $\alpha - 0{\cdot}1°$ after four crystallisations. The *l*-base *d*-tartrate gave $\alpha + 1{\cdot}04°$ ($l = 2$) in 4% aqueous solution.

The *l*-base liberated from the tartrate had at 18° $[\alpha]_{5461} - 48{\cdot}2°$, $[\alpha]_{5790} - 42{\cdot}4°$; $[\alpha]_{5461} - 55{\cdot}3°$ and $[\alpha]_{5790} - 49{\cdot}6°$ in 1·8% benzene solution; and $[\alpha]_{5461} - 34{\cdot}4°$ and $-26{\cdot}9°$ in 1·5% solution in 50% and 20% aqueous alcohol, respectively.*

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CAMBRIDGE. [*Received, December 15th*, 1924.]

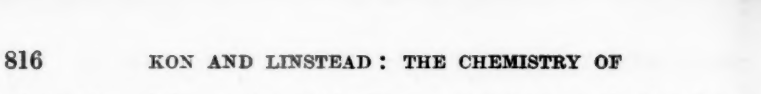
CXVI.—*The Chemistry of the Three-carbon System. Part IV. A Case of Retarded Mobility.*

By GEORGE ARMAND ROBERT KON and REGINALD PATRICK LINSTEAD.

THE cases of tautomerism considered in Part III. (this vol., p. 616) fall into a category exhibiting but a small degree of mobility, whilst those formerly described belonged essentially to a group possessing a very mobile tautomeric system. Thus *cyclo*hexenylacetone prepared by the Blaise-Maire reaction from the chloride

* The above values agree with those of Loven for the free base (40·16° for the D line) and of Kipping and Hunter (J., 1903, **83**, 1149), who obtained the value −25° in aqueous solution clarified by alcohol. The values have not hitherto been correlated, the resolutions having been carried out by different methods.

of *cyclo*hexylideneacetic acid (I) was identical with the ketone derived from the chloride of Δ^1-*cyclo*hexenylacetic acid (II):



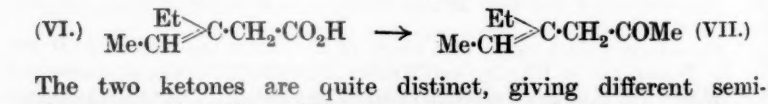
(I.) $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C{:}CH\cdot CO_2H \rightarrow$

$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\text{--}CH\end{matrix}>C\cdot CH_2\cdot COMe \leftarrow CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\text{--}CH\end{matrix}>C\cdot CH_2\cdot CO_2H$ (II.)

The conditions under which the synthesis was carried out precluded the possibility of previous isomerisation on the part of the acid chloride used. The same ketone is also obtained by condensation of *cyclo*hexanone with acetone and by the distillation of calcium *cyclo*hexanediacetate. It follows, therefore, that, whichever form is first produced in these reactions, the double linking assumes the stable position so rapidly that one and the same substance—or equilibrium mixture of constant composition and properties—is isolated. We wish to emphasise that the equilibrium between the two forms of *cyclo*hexenylacetone is established, apparently, in the absence of a reagent and is not dependent on the presence of, say, sodium ethoxide as suggested by Farmer (J., 1923, **123**, 3324), although his remarks apply to a number of other cases studied by us.

There is, however, no reason why the mobility of a three-carbon system should not be reduced (by substitution, etc.) to such an extent that the above condition is realised. The substance would then be capable of isolation in two distinct forms—an $\alpha\beta$ and a $\beta\gamma$—but these would be converted one into the other in the presence of a mild reagent or form an equilibrium mixture similar to those observed in cases of keto-enol tautomerism. Certain substances will now be described which satisfy this condition and are particularly interesting because they occupy as it were the border line between the two classes of tautomeric substances—they display retarded mobility.

When the chlorides of the two acids IV and VI (see Part III, *loc. cit.*) are treated with zinc methyl iodide, they give rise to the ketones V and VII, the latter being identical with that produced by the distillation of calcium $\beta\beta$-diethylglutarate (Kon, J., 1921, **119**, 810).

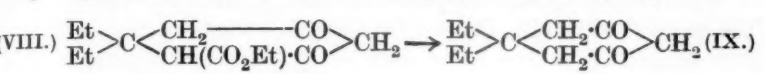


(IV.) $\begin{matrix}Et\\Et\end{matrix}>C{:}CH\cdot CO_2H \rightarrow \begin{matrix}Et\\Et\end{matrix}>C{:}CH\cdot COMe$ (V.)

(VI.) $\begin{matrix}Et\\Me\cdot CH\end{matrix}>C\cdot CH_2\cdot CO_2H \rightarrow \begin{matrix}Et\\Me\cdot CH\end{matrix}>C\cdot CH_2\cdot COMe$ (VII.)

The two ketones are quite distinct, giving different semicarbazones and yielding different oxidation products in accordance with the constitutions assigned to them; (V) also shows the expected

exaltation of the molecular refraction. The two compounds are, therefore, non-tautomeric under the conditions of the Blaise-Maire synthesis, in striking contrast to the case of *cyclo*hexenylacetone. In presence of sodium ethoxide, however, the three-carbon system in these compounds becomes more mobile and the ketone (VII) condenses with ethyl sodiomalonate just as readily as its isomeride, giving the ester (VIII), which passes on hydrolysis into the beautifully crystalline 3 : 5-*diketo*-1 : 1-*diethyl*cyclo*hexane* (IX).



(VIII.) (IX.)

It is obvious that an equilibrium must first be established between the two forms and as the αβ-form reacts more of it is produced until the reaction is complete.

This equilibrium is established slowly in the absence of a reagent with which the αβ-form can combine; thus, for instance, only 15% conversion can be detected in 24 hours in the presence of sodium ethoxide alone. The converse change, however, is more rapid, some 30% of the βγ-form being produced from the αβ under the same conditions. The study of this change is considerably complicated by the fact that the semicarbazones of the two ketones, which should afford a ready means of separation, form eutectic mixtures which cannot be separated into their components without great difficulty. One such eutectic, containing about 80% of the αβ-form, has a definite crystalline form, melts at 121—122°, and has been prepared synthetically by crystallising a suitable mixture of the two components. The result of the above experiments shows clearly, however, that the βγ-form of the ketone is the more stable and it may be mentioned that the αβ-form is apparently quantitatively converted into the βγ by the action of dilute sulphuric acid; the change appears to be irreversible. The effect on the βγ-form of the addition and subsequent elimination of hydrogen bromide leads to a similar conclusion, because the ketone is recovered unchanged whereas in the cases studied by Blaise (*Bull. Soc. chim.*, 1905, **33**, 43) the βγ-form was completely isomerised to the αβ by similar treatment. Repeated attempts were made to alkylate the ketone (VII), but without success.

It appeared to be of interest to compare the ketones (V) and (VII) with the closely related *cyclo*pentenylacetone (XI) which had already been prepared by the distillation of calcium *cyclo*pentane-diacetate (Kon, *loc. cit.*). On treating the chlorides of the two isomeric acids (X) and (XII) with zinc methyl iodide, one and the same ketone was obtained, identical in every respect with the substance previously prepared.

(X.) $\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!\!>\!C{:}CH\cdot CO_2H$ $\begin{matrix}CH_2\cdot CH_2\\ CH_2\!-\!CH\end{matrix}\!\!>\!C\cdot CH_2\cdot COMe$ (XI.)

(XII.) $\begin{matrix}CH_2\cdot CH_2\\ CH_2\!-\!CH\end{matrix}\!\!>\!C\cdot CH_2\cdot CO_2H$

This ketone appears to possess the $\beta\gamma$-structure (XI) under ordinary conditions, but it is capable of reacting in the $\alpha\beta$-form because it condenses with ethyl sodiomalonate to give an 85% yield of the corresponding dihydroresorcinol derivative (Norris and Thorpe, J., 1921, **119**, 1199). On the other hand, it readily undergoes alkylation in the same way as *cyclo*hexenylacetone, a 35% yield of an α-ethyl derivative being obtained; as a matter of fact, no unchanged *cyclo*pentenylacetone is isolated in this reaction, the by-products consisting of high-boiling oils doubtless formed as the result of internal condensation.* The ketone is thus in every way analogous to *cyclo*hexenylacetone; the three-carbon system in this substance possesses a high degree of mobility, thus differing from the otherwise very similar open-chain ketones (V) and (VII). The difference is doubtless bound up with the great tendency for a double linking to migrate towards a five- or six-membered alicyclic ring, although the precise significance of this is not yet apparent; it is hoped that the study of a number of related phenomena which is at present in progress will shed further light on the subject.

Experimental.

δ-Ethyl-Δγ-hexen-β-one (V). — Pure ββ-diethylacrylyl chloride (see Part III.) was added to zinc methyl iodide in benzene, and the ketone (yield 64%) was isolated as described in Part I (J., 1923, **123**, 1361). The pure ketone regenerated from the semicarbazone boiled at 59°/14 mm., 164°/770 mm., and had $d_4^{17.9°}$ 0·85633, $n_D^{17.9°}$ 1·45223, $[R_L]_D$ 39·75 (calc. 38·72); it had a powerful odour reminiscent of that of mesityl oxide. The ketone did not give a colour with alcoholic ferric chloride.

The *semicarbazone* crystallised from ethyl acetate–petroleum in flattened needles, m. p. 159° (Found: C = 59·3; H = 9·6; N = 23·2. $C_9H_{17}ON_3$ requires C = 59·0; H = 9·3; N = 22·9%). A semicarbazide-semicarbazone could not be obtained.

The ketone was oxidised with cold 3% potassium permanganate solution in the presence of sodium hydrogen carbonate. The diethyl ketone obtained in the neutral fraction of the oxidation product was identified by means of its *p*-nitrophenylhydrazone,

* We were unable to introduce a methyl group into *cyclo*pentenylacetone under similar conditions; the methylated ketone was, however, prepared in small quantity by the action of magnesium methyl iodide on *α-cyclo*pentylidenepropionitrile (Birch and Kon, J., 1923, **123**, 2440).

m. p. 137°, whilst oxalic acid constituted the acid fraction. Diethyl ketone was also produced by the action of ozone. The ketone (5·3 g.) was condensed with ethyl sodiomalonate under the conditions used by Norris and Thorpe (*loc. cit.*), 8·7 g. of the crude ester being obtained. This could not be induced to crystallise and was therefore hydrolysed with barium hydroxide, 3·5 g. (50%) of *diethyldihydroresorcinol* (IX) being obtained; this crystallised readily from benzene and light petroleum in flattened needles, m. p. 113° (Found: C = 71·1; H = 9·5. $C_{10}H_{16}O_2$ requires C = 71·4; H = 9·6%).

δ-Ethyl-Δ$^{\delta}$-hexen-β-one (VII).—This substance was prepared (yield 68%) in exactly the same way as its αβ-isomeride, using the chloride of β-ethyl-Δ$^{\delta}$-pentenoic acid. It was isolated in the form of its semicarbazone, m. p. 144—145° after purification; this proved to be identical with the semicarbazone previously obtained by Kon (*loc. cit.*). The ketone regenerated from it had b. p. 57°/13 mm., 163—164°/756 mm., $d_4^{19\cdot6°}$ 0·85883, $n_D^{19\cdot6°}$ 1·44301, $[R_L]_D$ 38·93; it gave no colour with alcoholic ferric chloride.

The ketone, dissolved in chloroform, was treated with ozone, and the ozonide decomposed by warming with water and finally distilling in steam, when a good yield of acetaldehyde (isolated in the form of the condensation product with β-naphthol; see Part III., *loc. cit.*) was obtained; no trace of diethyl ketone could be detected in the volatile portions of the oxidation product. The residue in the flask gave an intense red colour with alcoholic ferric chloride and formed a copper compound, crystallising from alcohol in blue-grey needles, m. p. 197°, and probably consisted of propionylacetone.

The ketone was unchanged after treatment with sodium ethoxide and ethyl iodide in excess.

The condensation with ethyl sodiomalonate was carried out exactly as described for the αβ-ketone; the yield of diethyldihydroresorcinol was precisely the same (50%).

Interconversion of the αβ- and βγ-Ketones.—The pure βγ-ketone (2·5 g.) was mixed with a cold solution of 0·5 g. of sodium in 10 c.c. of alcohol and kept for 28 hours. Water was then added, the ketone isolated by means of ether and converted into the semicarbazone, which was fractionally crystallised from ethyl acetate–light petroleum (b. p. 40—60°). The first crop of crystals consisted of the βγ-semicarbazone (m. p. 138°; m. p. of mixture with pure βγ-semicarbazone 142°; with αβ-semicarbazone, 121°). The second and subsequent crops were composed of a substance forming definite needles, m. p. 121—122° (unchanged by recrystallisation). The addition of the αβ- or βγ-semicarbazone raised the melting point to 135—140°.

The same eutectic mixture of semicarbazones was prepared by mixing known quantities of the αβ- and βγ-ketones, converting the mixture into the semicarbazone, and fractionally crystallising the latter. By carefully collecting and weighing the different crops of crystals obtained, it was estimated that the eutectic mixture contains about 80% of the αβ- and 20% of the βγ-semicarbazone. From the quantity of βγ-semicarbazone and eutectic mixture obtained, the amount of isomerisation of the βγ-ketone to the αβ in the above experiment appears to be about 15%. In a simultaneous experiment carried out with the pure αβ-ketone, the amount of conversion was about 35%.

The βγ-ketone (4·2 g.) was added to 6 g. of hydrobromic acid saturated at 0°, the mixture being kept cold; after 15 minutes, it was poured into water and extracted with ether, the extract being washed, dried, and evaporated. The bromo-ketone was obtained as a heavy liquid with an odour resembling that of eucalyptus oil; it did not combine with semicarbazide. The crude substance was boiled with a solution of 5 g. of potassium hydrogen carbonate in 30 c.c. of water for about 2 hours, and the ketone was recovered in the usual way and converted into the semicarbazone. The latter proved to be the semicarbazone of the βγ-ketone accompanied by a small quantity of the eutectic mixture; it is estimated that no more than 5% conversion to the αβ-form had occurred.

The αβ-ketone (2·5 g.) was boiled with 6 c.c. of 25% sulphuric acid under reflux; the ketone was then isolated and converted into the semicarbazone. This proved to be the pure βγ-compound, the isomerisation being complete. A similar experiment was carried out with the βγ-ketone, the substance being recovered unchanged.

Δ^1-*cyclo*Pentenylacetone (XI).—Δ^1-*cyclo*Penteneacetic acid was prepared by Wallach's method (*Annalen*, 1906, **347**, 324) and converted into the *acid chloride*, b. p. 75°/23 mm. This was treated with zinc methyl iodide in the usual way, giving a 58% yield of the ketone, which was usually contaminated by an unpleasant-smelling impurity removable by repeated extraction with potassium hydroxide solution. The semicarbazone was readily obtained and could be separated into two forms, melting at 189° and 138°, respectively, and identical with the two semicarbazones obtained by Kon (*loc. cit.*). The ketone regenerated from the semicarbazone boiled at 69°/11 mm., 186°/765 mm., and had $d_4^{19°}$ 0·9373, $n_4^{19°}$ 1·47291, $[R_L]_D$ 36·91.

The same ketone was also obtained in 50% yield, starting with *cyclo*pentylideneacetic acid (Harding and Haworth, J., 1910, **95**, 480; compare Part III.), the *chloride* of which was found to

boil at 69°/13 mm. The ketone gave the two semicarbazones melting at 189° and 138° respectively, these being identical with the semicarbazones of the ketone prepared from calcium *cyclo*pentanediacetate.

No isomerisation occurred on converting either the αβ- or the βγ-acid into its chloride, because the original acid could be regenerated from it.

α-*Ethyl*-Δ^1-cyclo*pentenylacetone*, $\begin{matrix}CH_2{\cdot}CH_2\\ |\\ CH_2{-}CH\end{matrix}\!\!>\!C{\cdot}CHEt{\cdot}COMe$.—The ethylation of *cyclo*pentenylacetone was carried out exactly as in the case of the higher homologue (Part I, *loc. cit.*). A fraction boiling between 70°/16 mm. and 86°/14 mm. (mainly 84—86°/14 mm.) was obtained in 35% yield, and this did not appear to contain any unchanged original material. It reacted at once with semicarbazide acetate, giving the *semicarbazone* of the α-ethyl derivative of *cyclo*pentenylacetone; the semicarbazone was somewhat sparingly soluble in alcohol, from which it separated in colourless plates, m. p. 167° (Found: C = 63·1; H = 9·6. $C_{11}H_{19}ON_3$ requires C = 63·1; H = 9·2%).

*cyclo*Pentenylacetone could not be methylated by the action of methyl iodide and sodium methoxide, the original ketone being recovered unchanged. The α-methyl derivative was, however, prepared in small amount by the following process: α-*cyclo*Pentylidenepropionitrile (8 g.) (Birch and Kon, *loc. cit.*) was added to an excess of magnesium methyl iodide in ether. When the vigorous reaction had subsided, the mixture was warmed for an hour, the magnesium compound decomposed in the usual manner, and the volatile products distilled in steam and isolated by means of ether. They consisted of the new ketone together with a considerable amount of unchanged nitrile. The ketone was converted into its *semicarbazone*, the adhering nitrile being removed by means of light petroleum. The semicarbazone separated from dilute methyl alcohol in glistening plates, m. p. 181—182° (Found: C = 61·8; H = 9·05. $C_{10}H_{17}ON_3$ requires C = 61·5; H = 8·8%).

The authors' thanks are due to the Chemical Society for a grant which has partly defrayed the cost of this investigation; and to Mr. Grant of this College for his help in the preparation of some of the materials used.

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CXVII.—*The Photodecomposition of Chlorine Water and of Aqueous Hypochlorous Acid Solutions. Part I.*

By Arthur John Allmand, Percy Walmsley Cunliffe, and Robert Edwin Witton Maddison.

Since Berthollet's discovery that chlorine water is decomposed when exposed to light, with evolution of oxygen and formation of hydrochloric acid, many papers have been published on the subject. None of these, however, deals with the reaction in a systematic fashion, and the present work, carried out during 1921—1924, is an attempt to fill up some of the gaps in our knowledge of this photolysis. The literature is too voluminous to give fully here. The majority of the papers are quoted in Mellor's "Inorganic and Theoretical Chemistry," Vol. II, p. 78. Other papers dealing with the reaction are those by McLeod (J., 1886, **49**, 608), Richardson and others (*Rep. Brit. Assoc.*, 1888, 89; 1889, 59; 1890, 263), Richardson (J., 1891, 59, 536), and Benrath and Schaffganz (*Z. physikal. Chem.*, 1922, **103**, 139). Little has been published on the photodecomposition of solutions of hypochlorous acid. Gay-Lussac (*Annalen*, 1842, **43**, 153) and Williamson (*ibid.*, 1855, **54**, 133) both refer to the acid as being photosensitive. Foerster and Jorre (*J. pr. Chem.*, 1899, **167**, 81) confirm this, whilst stating that the photosensitivity is small. Pedler (J., 1890, **57**, 613) carried out a few experiments on the subject, Clark and Iseley (*J. Ind. Eng. Chem.*, 1920, **12**, 1116) state that its photodecomposition in sunlight is monomolecular, and finally, a few observations are recorded by Benrath and Schaffganz (*loc. cit.*).

With respect to the decomposition of chlorine water, the main results of previous work can be summarised as follows. The reaction in the dark is inappreciable (Draper). The products of the photoreaction are generally given (more particularly in the earlier papers, though this is also the case in the quite recent work of Benrath and his pupils) as merely hydrochloric acid and oxygen. Popper (1885) was the first to notice that chloric acid can be formed in quantity. This observation was confirmed by Gore (1889), Klimenko (1889 and later), Pedler (1890), and Billitzer (1906), the formation of oxygen, according to the last author, being quite unimportant. Billitzer reports the production of perchloric acid, and Gore mentions hydrogen peroxide. According to Richardson (1891), the evolved oxygen is ozonised, but no hydrogen peroxide is produced. The presence of hydrochloric acid renders chlorine water far less sensitive (Bunsen and Roscoe and other subsequent workers), although, according to Billitzer, a *small* addition of acid acts as a positive

catalyst. The addition of other chlorides also retards the reaction, although less effectively than hydrochloric acid (Klimenko, Billitzer, Milbauer); so also do certain sulphates (Benrath and Schaffganz). Bromine acts as a positive catalyst (Milbauer). The evolution of the oxygen is subject to marked supersaturation effects (Berthollet). As will be seen, this circumstance probably accounts for the induction period and the " after effect " noted by Draper. The reaction goes more readily in violet light than in the rest of the visible spectrum (Davy). The temperature coefficient is 1·4 (Benrath and Tuchel).

De Saussure, assuming the validity of the $I \times t$ law, recommended the use of chlorine water as an actinometer liquid. According to Wittwer, the reaction is of the first order, and its rate is proportional to the intensity of the light. Bunsen and Roscoe, and, later, Billitzer, found no such relations, Billitzer saying that the reaction is autocatalytic. Finally, the actual primarily photosensitive constituent is imagined to be chlorine itself (earlier workers and Billitzer), hypochlorous acid (Pedler, Pebal, Jakowkin, Klimenko, and more particularly Dawson), and the ClO' ion (Benrath and Schaffganz).

Plan of Work.—It will be seen that, not only is there disagreement as to the mechanism of the reaction, but there are discordant statements even as to the chemical nature of the reaction products. No work has been done in monochromatic light, and the energetics of the reaction has not been touched. It is therefore to these points in particular that our attention has been directed.

The present paper is an account of our work on the reaction products and the factors affecting them. We adopted a working hypothesis which we subsequently found to have been previously developed up to a point by Jakowkin (*Z. physikal. Chem.*, 1899, 29, 621) and by Dawson (*Z. wiss. Phot.*, 1914, **14**, 213). A solution of chlorine in water is, at the ordinary temperature, very considerably hydrolysed (Jakowkin, *loc. cit.*) according to the equation,

$$Cl_2 + H_2O \rightleftarrows HClO + H^{\cdot} + Cl'.$$

All evidence goes to show that the addition of chlorides and, in particular, of hydrochloric acid, retards its photodecomposition. This follows qualitatively from the above equation if the hypochlorous acid molecule is considerably more photosensitive than the chlorine molecule. It would appear reasonable to suppose that the primary decomposition reaction in the case of hypochlorous acid would be

$$HClO \longrightarrow HCl + O$$

and also that oxygen atoms would be formed at an early stage when

chlorine was the photosensitive substance. (Possible reaction mechanisms will be considered more closely in the second paper). The production of molecular oxygen and chloric acid would then be due to secondary reactions, the latter substance being formed as a result of the hypochlorous acid molecules acting as acceptors for the oxygen atoms. If, therefore, by addition of suitable non-photosensitive substances, it could be arranged practically to exclude the presence from the solution during insolation of either hypochlorous acid molecules or of chlorine molecules respectively, one might expect in the first case a slow reaction with very little chlorate formation, and, in the second case, a more rapid reaction with a higher percentage of chloric acid in the product than would have been the case with ordinary chlorine water.

The addition of either hydrogen ions or chlorine ions to chlorine water will increase the chlorine concentration in the solution at the expense of that of the hypochlorous acid. Experiments were accordingly carried out with chlorine water in which the percentages of the reaction products were carefully estimated. Similar experiments were then done with chlorine dissolved in solutions of potassium chloride, lithium chloride, cadmium chloride, sulphuric acid, and hydrochloric acid of varying strengths, in order to study the effect of hydrogen ions and chlorine ions, separately and in conjunction with each other. Experiments were further done with chlorine dissolved in solutions of sodium sulphate and lithium sulphate, in order to test the effect of neutral salts, and with chlorine dissolved in bromine water and in solutions of copper sulphate, cobalt sulphate, and nickel sulphate, in connexion with later experiments on possible catalytic effects.

With the intention of affecting the Jakowkin equilibrium in favour of hypochlorous acid, experiments were carried out with chlorine water containing dissolved mercuric chloride, the idea being that, as the result of the reaction

$$HgCl_2 + 2Cl' \longrightarrow HgCl_4'',$$

the hydrolysis of chlorine would be made almost complete. Subsequent reference to Sherrill's work (*Z. physikal. Chem.*, 1903, **43**, 734; 1904, **47**, 103) showed this not to be so, only a moderate diminution in chlorine-ion concentration being effected even by saturating the chlorine water with mercuric chloride. Measurements of Jakowkin himself led to the same conclusion.

A solution of hypochlorous acid, on insolation, immediately forms hydrochloric acid, with consequent production of chlorine in the solution. To avoid this, it is necessary to remove either the chlorine ions or the hydrogen ions as they are formed. Experiments

were done with addition of mercuric chloride to remove the chlorine ions. They were few in number, not very concordant, and are not recorded here, more particularly as, for the reason just stated, they were ill-adapted to achieve their purpose. In order to remove the hydrogen ions, the obvious course was to add to the solution the sodium salt—NaR—of a weak acid unaffected by light. The acid chosen, however, should not be so weak as to allow of the reaction

$$HClO + R' \longrightarrow ClO' + HR$$

setting in, as the photosensitivity of the sodium hypochlorite formed would then complicate matters. The necessary condition is that the salt used should be of an acid with a dissociation constant which, whilst small, is appreciably greater than that of hypochlorous acid. Sodium acetate and disodium hydrogen phosphate were chosen, and the products of photodecomposition in their presence investigated. Any formation of hypochlorite ion will take place according to the respective equations

$$HClO + Ac' \longrightarrow HAc + ClO'.$$
$$HClO + HPO_4'' \longrightarrow H_2PO_4' + ClO'.$$

The dissociation constants K_{HAc} and $K_{H_2PO_4'}$ (Abbott and Bray, *J. Amer. Chem. Soc.*, 1909, **31**, 729) are respectively $1{\cdot}8 \times 10^{-5}$ and $1{\cdot}95 \times 10^{-7}$ at 18°. The value for K_{HClO} is given as $3{\cdot}7 \times 10^{-8}$ (Sand, *Z. physikal. Chem.*, 1904, **48**, 610), $6{\cdot}7 \times 10^{-10}$ (Noyes and Wilson, *J. Amer. Chem. Soc.*, 1922, **44**, 1630), and 1×10^{-8} (Soper, J., 1924, **125**, 2227). When starting these particular experiments, we assumed the figure given by Noyes and Wilson to be probably more nearly correct than that of Sand, in which case the condition necessary for practical non-formation of hypochlorite ions would be satisfied. It would seem, however, from Soper's work, that their value is certainly too low. Adopting the figure of 1×10^{-8}, an approximate calculation shows that, in a solution containing $M/8$-Na_2HPO_4 + $M/20$-HClO, about 28% of the hypochlorous acid is present as hypochlorite ions, and that this proportion is reduced to about 15% when the solution is half decomposed. Our results must therefore be considered in the light of this uncertain factor. With sodium acetate, no such difficulty arises, and the production of both hydrogen- and hypochlorite-ions should be satisfactorily repressed.

Experimental.

Preparation of Solutions.—Chlorine was prepared by the action of concentrated hydrochloric acid on either potassium dichromate or potassium permanganate crystals, the gas being washed by water (in the latter case also by a solution of potassium permanganate

prior to the water washing) and then passed into distilled water or into the appropriate solution. Hypochlorous acid was prepared by the method of Bostock and Taylor (J., 1912, **101**, 451), *viz.*, by distillation at a pressure of about 120—140 mm. of a mixture of bleaching powder, boric acid, and water. In some cases a solution of sodium hypochlorite was substituted for the bleaching powder. Unless the pressure were lowered well below the figure just given, the distillate was appreciably weaker, in spite of the higher hypochlorite concentration in the distilling flask. This difference is presumably due to the relative insolubility of the calcium borate resulting in the first case, and to boric acid being a weaker acid than hypochlorous acid (accepting Soper's figure for K_{HClO}). When insolating mixtures of hypochlorous acid and the above-mentioned salts, weighed quantities of the latter were dissolved in the hypochlorous acid solution.

Analytical Methods.—During the whole of the work, as will be seen later, the only decomposition products found, apart from hydrochloric acid, were chloric acid and oxygen.* In what follows, the concentrations of the different oxidising substances concerned are expressed as normalities of equivalent oxidising power. Thus "normal" solutions of chlorine, hypochlorous acid, and chloric acid contain respectively 35·5, 26·2, and 14·1 g./litre of the substance concerned. In the particular case of oxygen, supposing it to remain in solution, a normal solution would contain 8 g./litre, and it can be readily seen that, in correlating the quantity of oxygen produced during a given experiment with the corresponding loss in chlorine or hypochlorous acid, the following equation holds:

$$\text{"Normality" of oxygen} = 4v/22{\cdot}4V,$$

where V is the volume of the insolated solution, and v the volume of evolved oxygen at N.T.P.

Chlorine and hypochlorous acid were determined by delivering a known volume of the solution under the surface of an acidified 5% solution of potassium iodide, and titrating with $N/10$-thiosulphate. A special experiment showed that solutions containing hydrochloric and chloric acids at concentrations of the order of those prevailing after insolation caused no detectable liberation of iodine from the potassium iodide. Owing to the volatility of chlorine, concordant results could only be obtained if great care were exercised during pipetting and transference. In the later work, the pipette designed by Jakowkin (*loc. cit.*) was used with advantage.

Chloric acid was determined by the Bunsen method, using

* The paper of Richardson, in which the formation of ozonised oxygen is recorded, was not read until this work was finished, and the point has not yet been tested.

N/10-ferrous sulphate and N/10-potassium permanganate solutions. A certain amount of trouble was experienced at the start in dealing with *partly* decomposed solutions containing both free chlorine and chloric acid. Attempts to determine chlorine plus chlorate by the ferrous sulphate method failed. Titration of chlorate by titanous chloride gave an unsatisfactory end-point, the percentage error involved being too great in the case of the dilute solutions used. We then investigated the addition of substances which would destroy the hypochlorous acid or chlorine present, without either attacking the chlorate or leaving behind in the solution something which would subsequently vitiate the chlorate determination (as was the case when the chlorine was titrated with potassium iodide and sodium thiosulphate or with sodium arsenite). Manganous sulphate, urea, and oxalic acid were all found to be possible reagents. Oxalic acid was chosen, as it seemed feasible that, by its use, both Cl_2(HClO) and $HClO_3$ might be determined on a single sample. The general procedure was to pipette 10 c.c. of the solution into a conical flask, to add 20—40 c.c. of N/10-oxalic acid, and to warm *slowly* until nearly boiling, adding about 20—30 c.c. of dilute sulphuric acid towards the end of the heating, which should take at least 10 minutes. The excess of oxalic acid was then titrated with N/10-permanganate to a faint pink colour, and the chloric acid determined in the usual way. Appropriate experiments showed (*a*) that no formation of chloric acid took place during the reduction of the Cl_2(HClO), and (*b*) that, with the concentrations used, the above procedure resulted in no loss of chloric acid by interaction with the oxalic acid, as is the case with stronger solutions (Bray, *Z. physikal. Chem.*, 1906, **54**, 463, 569, 731). Losses of the order of 5—10% of the total soon, however, appeared if the solutions were too concentrated or too rapidly heated during the oxalic acid treatment, and, until this was appreciated, concordant results were not obtained.

Further experiments showed that the presence of mercuric chloride and of the other salts added during the work did not affect the accuracy of the chlorate determination, with the exception of 2N-sodium acetate, when the results were about 1% too low. It was mentioned above that it seemed possible to determine both chlorate and HClO(Cl_2) *on the same sample* by this method, the condition being of course quantitative oxidation of the oxalic acid according to the equations

$$H_2C_2O_4 + HClO \longrightarrow HCl + 2CO_2 + H_2O$$
$$H_2C_2O_4 + Cl_2 \longrightarrow 2HCl + 2CO_2.$$

Using an *uninsolated* solution of hypochlorous acid, this was found to be the case, very concordant results being obtained from

analyses by the oxalic acid, iodide and thiosulphate, and sodium arsenite methods. With *insolated* solutions of hypochlorous acid or with chlorine water, however, the results were found to average about 4% too low, due in all probability to volatilisation of chlorine before complete reaction. In the great majority of the experiments, including all those carried out with chlorine water, separate samples were used for the $Cl_2(HClO)$ and $HClO_3$ determinations.

Dark Experiments.—The following solutions, of oxidising power varying between 0·05*N* and 0·12*N*, were sealed up in glass tubes, kept in the dark for periods varying between 2 and 20 days, and subsequently titrated: Hypochlorous acid dissolved in water, in *M*/4-disodium hydrogen phosphate and in *N*/2-sodium acetate; chlorine dissolved in water and in 5% mercuric chloride, 10% nickel sulphate, 10% cobalt sulphate, and 5% lithium sulphate. As always, the greatest care had to be exercised in the manipulation and transference of the solutions containing chlorine, if significant results were to be obtained, these being very readily masked by volatilisation losses caused during pouring, pipetting, etc. The results showed losses in $Cl_2(HClO)$ titre varying between 0·002*N*—0·009*N* per 24 hours, except in the cases of the chlorine–cobalt sulphate and hypochlorous acid–sodium acetate mixtures. Such small figures show that the dark reaction can be neglected when carrying out the light experiments. In the case of the two exceptions, the titre fell per day by amounts varying between 0·02*N*—0·075*N*. A black precipitate was formed in the cobalt sulphate solution. The results in the case of the hypochlorous acid–sodium acetate mixture will be quoted later.

Apparatus.—All the definitive experiments were carried out with 110-volt Cooper-Hewitt quartz mercury lamps of the straight tube pattern. Two kinds of insolation cell were used. The first and simpler type consisted of a clear silica flask of about 130 c.c. capacity, closed by a rubber stopper. In the first experiments, the light from the lamp passed successively through a 1 cm. quartz water-cell and an aperture in a hollow copper screen, a stream of water at constant temperature being taken through the screen and a copper condenser on the neck of the flask, finally running out over the surface of the flask to waste. It was found later that a stream of tap-water playing over the surface of the flask sufficed to keep the temperature constant. The rubber stopper carried two capillary tubes. One of these in the earlier experiments led down to the bottom of the flask, and was used for saturating the photolyte with oxygen beforehand, a process which was soon discontinued. It was closed by pressure tubing and a screw-clip during insolation. The second was fused on to a three-way tap at the top of a small, water-jacketed

gas burette, provided with a levelling tube and filled with potassium iodide solution. To avoid the manipulation errors already referred to, the chlorine solutions used were finally prepared in the flask, a sample being withdrawn for analysis before insolation.

In carrying out an experiment, the flask was almost filled with the solution under study, put into connexion with the gas burette, and the latter levelled off and read after temperature equilibrium had been reached. The lamp was then lighted, the insolation proceeded with, and burette readings taken at intervals. When the volumes of oxygen collected became too large, they were discharged into the air by the three-way tap, and readings re-started without interrupting the insolation. Sometimes this was carried to completion—sometimes interrupted for a few moments in order to pipette out a sample for analysis, in which case it was necessary to disconnect the burette from the flask. At the end of the experiment, any iodine liberated from the potassium iodide in the burette by chlorine carried over with the oxygen was titrated, and a correction applied.

A large number of experiments were done with this apparatus. The use of a rubber stopper is open to objection. The necessity of disconnecting flask and burette for the purpose of withdrawing a sample for analysis was a disadvantage. So also was the comparatively large dead-space left in the apparatus after removing a sample for titration before insolation, as the chlorine contained in the vapour phase thus produced only slowly diffused along into the potassium iodide solution in the gas burette, rendering the correction correspondingly uncertain. The results were less concordant amongst themselves than those obtained with the cell now to be described, although agreeing sufficiently with the latter.

The cell used in the later experiments consisted of a rectangular glass block $10 \times 10 \times 5$ cm., through which had been drilled a horizontal cylindrical hole, 7·5 cm. in diameter. This hole was closed back and front by circular windows of crystal quartz, cemented to the plane surface of the glass block by a hard pitch composition, special experiments showing that no appreciable reaction took place between dissolved chlorine and the very small surface of cement exposed to its action. In the top of the cell, two openings were drilled. One, closed by a ground-glass stopper, served for the introduction of a pipette for taking samples, etc. The other was closed by a water-sealed, ground-glass joint, bearing a capillary tube connexion sealed on to the gas burette. A similar cell, 2 cm. in depth, served as a water-filter to cut out heat rays. In some experiments, it was directly attached to the front quartz plate of the reaction vessel, thus forming a compound cell, and economising a quartz plate. Experiments showed that, in this

case, there was never more than 0·5° difference between the temperature of the water flowing through the filter and that of the liquid in the reaction cell.

As the work proceeded, continual minor improvements in technique were made. The most concordant results were obtained when the dead-space in the insolation cell was reduced to a minimum (about 3 c.c.).* The solution under investigation was prepared in a stock bottle, and siphoned off into the cell. The latter was first of all rinsed out several times with about 10 c.c. of the liquid, and a vapour phase thus established. It was then filled and, after pipetting out 20 c.c. for analysis, refilled from the stock bottle. In addition, the gas leaving the cell was caused to pass *through* two small traps containing potassium iodide solution, the gas burette being filled with water. After the completion of the experiment, any chlorine in the connecting tubes was gently blown through the potassium iodide traps, the first of which in practice sufficed for complete absorption.

Supersaturation Effects.—It was at first thought that it might be possible to follow the rate of reaction during insolation by means of the volume of oxygen collected at any instant, but it was soon found that this was out of the question, owing to the remarkable extent to which supersaturation occurred. The rate of evolution of gas was, of course, low at the start, owing to the necessity of first saturating the photolyte. It usually increased to a more or less constant value after 2—3 hours. If insolation were interrupted before complete decomposition, then gas continued to come off at the same rate for another 2—3 hours, and only after many hours' standing did the volume become constant. If insolation were continued until all the HClO(Cl_2) had reacted, the rate of collection of gas became less towards the end, corresponding with the decreased light absorption and rate of decomposition. But the liberation of oxygen after the light was cut off still persisted. Careful experiments showed that there was no change taking place in the electrolyte, the oxidising titre of which remained quite unaltered in the dark. The reaction therefore does not exhibit an "after effect." Saturation with oxygen beforehand made no essential difference, not even to the initial time required for the rate of gas evolution to become approximately constant.

The nature of the surface of the containing vessel, on the other hand, had an effect. Gas could be seen coming off at definite points

* At the beginning of the work the dead-space was carefully shielded from light, in order to avoid the possibility of the reaction $2Cl_2 + 2H_2O \longrightarrow 4HCl + O_2$ taking place in the vapour phase. Work done in another connexion in the laboratory showed this precaution to be unnecessary.

on the surface, and the delayed evolution was more marked with experiments carried out in the smooth silica flasks than was the case when using the composite cells with their inner surface of ground-glass. When sand or powdered quartzite was added to the insolation cell, the rate of gas evolution was still further increased, but its appearance in quantity subsequent to the insolation was never eliminated.

The consequence of the phenomenon was that the sum of the amount of oxygen collected as gas and of that contained in the chloric acid found after the experiment was very seldom (within the experimental error) equal to that calculated from the loss in titre of $Cl_2(HClO)$, even when the solution was left standing for hours after the experiment. The deficiency could easily amount to 30% of the whole. As the formation of perchloric acid had been reported by Billitzer, we tested for this substance in the insolated solution after neutralisation with alkali, using the reaction with methylene-blue described by Monnier (*Ann. Chim. Analyt.*, 1916, 20, 237). None was ever found, nor, it may be mentioned here, did the usual tests ever show the presence of hydrogen peroxide,* the formation of which had been mentioned by Gore. In order to get more positive evidence, experiments were done in which the solution was either allowed to stand for very considerable periods after the insolation, or in which the apparatus was vigorously shaken before the final reading was taken. The following are specimens of the results obtained.

Initial titre.	Final corrected titre.	Corrected loss in titre.	Titre of chloric acid formed.	Titre of oxygen.	Chloric acid plus oxygen.
0·095*N*-HClO	0·0025*N*	0·0925*N*	0·059*N*	0·032*N*	0·091*N*
0·0935*N*-Cl_2	0·0047*N*	0·0888*N*	0·0563*N*	0·0313*N*	0·0876*N*

It was further shown, on several occasions, that, after complete decomposition of a solution of hypochlorous acid, all the chlorine originally present as hypochlorous acid (allowing for losses by volatilisation) was to be found in the solution either as chloric acid or as hydrochloric acid, thus showing that any formation of perchloric acid was negligible. It seems therefore reasonable to suppose that supersaturation is solely responsible for the observed phenomena, and that there is neither an "induction period" nor an "after-effect," as Draper had imagined.

Certain remarkable experiments should, however, be especially mentioned, in which chlorine water and chlorine water containing

* Observations of Anderson and Taylor (*J. Amer. Chem. Soc.*, 1923, 45, 1215) render it unlikely that appreciable amounts of hydrogen peroxide could exist under our experimental conditions.

dissolved mercuric chloride were insolated in a silica flask. Practically no gas could be seen coming off from the solutions during irradiation and, in the whole set of about twenty-five experiments, more than 2 c.c. of oxygen were never collected during any single insolation, although amounts of up to 50 c.c. would have been anticipated from the subsequent analyses for chloric acid and negative tests for perchloric acid. After completion of the experiments, the solutions were in some cases boiled or evacuated, but not more than an extra c.c. of gas was ever obtained. This curious non-appearance of gas remains unexplained. It is, of course, possible to imagine the gas being given off from the liquid surface as single molecules or small aggregates, instead of being liberated as visible bubbles. It is also true that the neck of the flask was closed by a rubber stopper, which might conceivably react with any "activated" oxygen or ozone, but the suggestion would seem inadequate to explain such a complete elimination of the appearance of oxygen. It may be added that of course the possibilities of a leak or of the presence of some reducing agent in the apparatus were carefully gone into. In any case, the striking feature of the experiments to the eye was the absence of visible oxygen evolution. It is hoped to follow up the subject further. In the meantime, it may be mentioned that relevant data are contained in the recent papers by Metschl (*J. Physical Chem.*, 1924, **28**, 427) and by Kenrick, Wismer, and Wyatt (*ibid.*, p. 1314).

Results.

The figures which follow represent the percentages of chlorine or hypochlorous acid which, on reaction, gave chloric acid as a product. The remainder, in absence of any positive test for perchloric acid or hydrogen peroxide, is assumed to have decomposed, giving oxygen.

Chlorine Water.—Several series of measurements, during which the experimental technique was gradually improved, were carried out, involving nearly fifty different insolations.

Series.	Type of apparatus.	No. of expts.	Extreme values.	Mean value.
1	Flask	9	56·3—68·3	62·5
2	Cell	6	57·4—62·3	60·1
3	Flask	3	58 —66	63
4	Flask	13	51 —76	60·4
5	Cell	3	55 —63	60
6	Cell	12	59 —63	61·3

The general mean is 61·2% of chloric acid, which is also practically the mean of the last and most concordant series. The strengths of the solutions insolated varied between 0·158*N* and 0·0175*N*, and

the degree of decomposition from about 15% to completion. The extreme values for the chloric acid figures were obtained either when the technique had not been fully developed, or when the titration values were very small, and the errors correspondingly great. We therefore feel justified in concluding that the proportions of the products are not sensibly affected either by the initial concentration or by the extent of decomposition.

*Chlorine in Hydrochloric Acid Solution.**—

Conc. of HCl	0·004*N*	0·01*N*	0·1*N*	0·5*N*
Chloric acid % ...	56	55·5	31·7; *29*; 27	22·5; 10; *14*

*Chlorine in Potassium Chloride Solution.**—

Conc. of KCl	0·1*N*	0·5*N*
Chloric acid %	51·9; *60*; 63; 45	44·3; *29*; 21; 15; 26

Chlorine in Mercuric Chloride Solution.—As with chlorine water, several series of measurements were done, the concentration of the mercuric chloride always being 5%. As aqueous mercuric chloride is reported by some observers to be photosensitive, with formation of calomel and evolution of oxygen (*e.g.*, Pougnet, *Compt. rend.*, 1915, **161**, 348), solutions containing the salt alone were insolated beforehand, but no trace of decomposition could be detected. This agrees with the observation of Lesure (*J. Pharm. Chim.*, 1910, **1**, 569).

Series.	Type of apparatus.	No. of expts.	Extreme values.	Mean value.
1	Flask	3	55—68	60·3
2	Flask	13	57—79	65
3	Cell	4	65—66	65·2
4	Cell	3	62—63·5	62·8

The general mean gives 64·1% of chloric acid.

Chlorine in other Chloride Solutions.—

Solution	0·01*M*-$CdCl_2$	0·1*M*-$CdCl_2$	0·5*M*-$CdCl_2$	0·5*N*-LiCl
Chloric acid %.....	55·7	57·9	44·6	39

Chlorine in Sulphuric Acid Solution.—

Conc. of H_2SO_4.	Chloric acid %.
0·1*N*	57·6; 64·2; 49·5; 62; 63; 57; 63 (mean figure 59·5)
0·5*N*	52·6; 48; 57; 59; 60; 61 (mean figure 56·3)

There appeared to be a certain tendency in this case for solutions containing higher initial chlorine concentrations to give lower chloric acid percentages.

* Many of the titration figures for chlorate were here exceedingly small —the percentages given in italics correspond to the largest, and hence presumably to the most trustworthy, titrations.

Chlorine in Sodium Sulphate Solution.—

Conc. of Na_2SO_4 ...	0·01*M*	0·1*M*	0·33*M*	Saturated
Chloric acid %	63·2	60·0	62·5; 62; 62	61·7

Mean figure 61·9

Chlorine in Lithium Sulphate Solution.—

Conc. of Li_2SO_4	0·25*M*	0·5*M*	1*M*	2*M*
Chloric acid %	63	67	69	73; 73

The colour of solutions of chlorine in aqueous sodium and lithium sulphates is far less pronounced than is the case with chlorine water alone, or with chlorine dissolved in dilute solutions of sulphuric acid or of halides.

Chlorine in other Solutions.—

Added solute	Bromine	0·5% $CuSO_4$	0·5% $CoSO_4$	0·5% $NiSO_4$
Chloric acid %	61·3	64; 63; 64	61·5; 56	59; 67

An experiment with chlorine dissolved in 0·5% manganous sulphate resulted in the rapid formation of a black precipitate, the same slowly occurring in the dark. In certain circumstances, the solution in cobalt sulphate behaved similarly.

Hypochlorous Acid.—Five experiments gave 65·3; 63·4; 57; 58; 60·2% of chloric acid (mean figure 60·8).

Hypochlorous Acid in Sodium Phosphate Solution.—Two experiments gave 81% in 0·25*M*- and 86% in 0·125*M*-disodium hydrogen phosphate.

Hypochlorous Acid in Sodium Acetate Solution.—It was mentioned earlier that experiment showed the dark reaction in this case to be considerable, a 0·1*N*-hypochlorous acid solution in 0·5*N*-sodium acetate losing about half its titre in 9 days. It soon became apparent that the light reaction itself was more complex than those hitherto studied. Two insolations were made of solutions of about the same composition as above. They rapidly lost their titre when exposed to light, but no evolution of oxygen could be detected in the one case, and the merest trace in the other, whilst subsequent analyses showed only 12 and 18%, respectively, of the original oxidising power as chloric acid. Chlorination or oxidation of the sodium acetate or of the acetic acid formed in the reaction naturally suggested itself, and the usual tests were applied for monochloroacetic, succinic, and oxalic acids. All were negative, although an appropriate amount of the substance concerned gave a positive result under the conditions of experiment. However, on boiling with alcoholic potash, after adding a drop of aniline, a faint but unmistakable smell of carbylamine was noticed, which pointed to the presence of chloroform. This observation probably means that hypochlorous acid chlorinates acetic acid or sodium acetate in light

to give trichloroacetic acid, the chloroform either being formed during the carbylamine test, or possibly being produced by the further action of light on the trichloroacetic acid *in statu nascendi*. The formation of the monochloro- and dichloro-acids is presumably transitory, as no trace of oxalic acid, which would be the final product of their photolysis under the experimental conditions, was found.

In order roughly to check the results, another insolation was carried out in which, after partial decomposition of the hypochlorous acid and determination of the chloric acid (which amounted to 24% of the loss in HClO titre), the chloride concentration of the solution which had been used in the chlorate analysis was determined by titration. The result, of course, represented the total chlorine present in the original solution, less that fixed (presumably) as trichloroacetic acid. The figures were (expressed as gram-atoms or gram-ions per litre)

	Cl in original HClO	0·0622
	Cl as HClO after insolation ...	0·0250
	Cl converted to $HClO_3$	0·0029
	Cl′ found on titration	0·0397
Hence	Cl as Cl′ after insolation	0·0397 − 0·0250 − 0·0029 = 0·0118
	Cl fixed as $CCl_3{\cdot}CO_2H$ (?) ...	0·0622 − 0·0397 = 0·0225

Another portion of the insolated solution was then taken, hydrolysed by 12·5% sodium hydroxide, and another chloride titration carried out. This figure (corrected for a blank test on the sodium hydroxide) should be a measure of the chloride formed during the insolation and by the hydrolysis, plus that produced on heating the alkaline sodium hypochlorite, in accordance with the reaction

$$3ClO' \longrightarrow 2Cl' + ClO_3'.$$

The result was 0·0542*N*. If we add the figures for the chlorine converted to chlorate ion during the insolation (0·0029*N*) and during the hydrolysis (0·0083*N*, if the above equation is correct), we get a total of 0·0654*N*, compared with the figure of 0·0622*N* in the 0·1244*N*-hypochlorous acid taken. The discrepancy of 5% is reasonable considering the assumptions made. Thus, for example, it is conceivable that, during the hydrolysis, further chlorination of the acetate by hypochlorite ions may have occurred, or possibly decomposition in accordance with the equation

$$2ClO' \longrightarrow 2Cl' + O_2,$$

either of which reactions would have caused a discrepancy in the sense found.

One further experiment was done, in which a dilute—0·5%—solution of sodium acetate was used, and the mixture with 0·045*N*-hypochlorous acid exposed to daylight for 10½ hours. The chloric

acid percentage of the loss in hypochlorous acid titre was now found to be 72, a very different figure from those given by strong sodium acetate solutions. Chloride determinations were carried out as above, and good agreement was found with the calculated figure. It would thus appear definitely as if, on insolating these solutions, two reactions proceed simultaneously—photodecomposition of the hypochlorous acid, resulting in the production of much chloric acid and little oxygen, and chlorination of the added acetate, the latter reaction naturally occurring to a greater extent the higher the percentage of acetate present. Time has not yet permitted of a further investigation of these results.

Effect of Wave-length.—Experiments carried out in sunlight, diffused daylight, and in monochromatic light of wave-lengths 313, 365, and 436 $\mu\mu$ showed no appreciable difference in the proportion of the products formed.

Effect of Surface.—Two experiments on solutions of hypochlorous acid indicated that, in presence of the highly developed surface furnished by adding pure silica powder to the contents of the insolation vessel, the proportion of chloric acid in the product was considerably reduced. In the present lack of confirmatory experiments, we prefer to lay no stress on this observation.

Discussion.

A detailed discussion of the mechanism of the reaction is best postponed until the measurements on the energetics have been described. Certain conclusions can, however, be drawn at this stage. The results obtained with the solutions of hypochlorous acid in disodium hydrogen phosphate, *viz.*, an increase in the chloric acid yield from 61 to 83%, support our assumption that oxygen atoms are the primary product of photolysis, and that molecules of hypochlorous acid present will act as acceptors for these oxygen atoms, or possibly for "activated" oxygen molecules, the final result being formation of chloric acid. That the addition of disodium hydrogen phosphate to the hypochlorous acid solutions did, in fact, prevent the formation of hydrochloric acid and thus of free chlorine during the insolation is made very probable by the fact that such solutions remained colourless throughout the experiment. Further, when chlorine was passed into a solution of disodium hydrogen phosphate, the initial yellow colour disappeared on standing for a short time, and on addition of potassium iodide, the solution behaved like hypochlorous acid, *i.e.*, it required added mineral acid in order to liberate its full amount of iodine. The uncertainty as to whether there was appreciable formation of hypochlorite *ions* has already been mentioned. One fact, however, speaks against this, as Mr.

M. Holmes, working in this laboratory on the photodecomposition of sodium hypochlorite solutions, found only 11—12% chlorate formation, indicating that hypochlorite ions are not very avid acceptors of oxygen atoms (or "activated" oxygen molecules). The results with sodium acetate solutions are perhaps less conclusive, in consequence of the simultaneous photochlorination which is going on. Nevertheless, the amount of oxygen set free in this case is negligible compared with the quantity of chloric acid produced. It is also noticeable that solutions of chlorine in aqueous lithium sulphate, which became more nearly colourless as the concentration of the salt was increased, gave corresponding progressively increasing yields of chloric acid.

When we consider the results obtained with chlorine water, however, particularly those given by solutions of chlorine in dilute hydrochloric acid, the facts by no means completely fit the original hypothesis. This was, briefly, that the only products, or practically so, of the photo-reaction between chlorine itself and water are *oxygen* and hydrochloric acid, and therefore that, if by addition of hydrochloric acid to the chlorine water beforehand, the amount of hypochlorous acid in the photolyte could be made negligible, there should be only a correspondingly minute quantity of chloric acid present after insolation. This, however, is not so.

The value of the Jakowkin equilibrium constant, $K = [Cl_2]/[H^{\cdot}][Cl^{\prime}][HClO]$, is about 2500 at 20°, concentrations being expressed as mols./litre (Gröh, *Z. physikal. Chem.*, 1913, **81**, 695; see also Lewis and Randall, "Thermodynamics," p. 508). Assuming complete dissociation of any hydrochloric acid added or formed by hydrolysis, we have calculated the approximate concentrations (before insolation) of the various constituents present in 0·1*N* (0·05*M*)-chlorine, dissolved in water and in 0·01*N*-, 0·1*N*-, and 0·5*N*-hydrochloric acid. The results are contained in the following table, together with the percentage yield of chlorate experimentally found :—

Solution insolated.	Fraction of chlorine hydrolysed.	[HCl].	[HClO].	[Cl_2].	Percentage chloric acid yield.
0·05*M*-Cl_2	0·45	0·0225	0·0225	0·0275	61
„ + 0·01*N*-HCl	0·35	0·0275	0·0175	0·0325	55*
„ + 0·1*N*-HCl	0·04	0·102	0·002	0·048	29†
„ + 0·5*N*-HCl	0·0015	0·500	0·000075	0·0499	14†

* One insolation only. † "Best" values.

It is clear that the chloric acid yield falls off far less rapidly than is likely to have been the case if it were solely produced by interaction between primarily formed oxygen and hypochlorous acid molecules present at concentrations demanded by the Jakowkin

constant. It would appear possible that hypochlorous acid is one of the intermediate products of reaction of photo-activated chlorine molecules with water, this photo-product acting as an acceptor for the oxygen. A somewhat similar mechanism was proposed by Billitzer. The effect of an increased concentration of hydrogen chloride would, of course, then be, by re-formation of chlorine, to lower the "stationary state" concentration of the hypochlorous acid, and thereby to decrease the opportunity for formation of chloric acid.

With regard to the results obtained with the other salts, addition of either potassium chloride, lithium chloride, or cadmium chloride lowers the chloric acid yield, but in a lesser degree than does hydrochloric acid, a result to be anticipated (qualitatively) from the Jakowkin equation. Potassium chloride would appear (in 0·5*N*-solution) to have the greatest effect, but the experiments are too few to enable any definite conclusions to be drawn. There is no doubt, however, that the action of sulphuric acid is, in this respect, much less than that of potassium chloride. This in itself is enough to show that the Jakowkin equation is by no means the only determining factor. The different ions appear to have specific effects, a view which is supported by the marked difference between the mode of decomposition of chlorine dissolved in sodium sulphate and in lithium sulphate solution.

From the figures with mercuric chloride solutions, we feel justified in concluding that the percentage of chloric acid is slightly increased. This result can be construed (qualitatively) in the light of the Jakowkin equation, as a rough calculation based on the results of Luther and of Sherrill shows that the chlorine-ion concentration in a completely photolysed 0·05*M*-chlorine solution is reduced by about half when the solution contains 5% of added mercuric chloride, owing to the formation of $HgCl_4''$ ions.

One further striking result should be commented upon. There is no doubt at all that the presence of small concentrations of hydrochloric acid (say 0·1*N* or less) added to chlorine-water solutions before insolation depresses the yield of chloric acid. On the other hand, no diminution in this yield during the insolation of a chlorine-water solution was ever observed, in spite of the fact that the concentration of hydrogen chloride was continually increasing. Still more remarkable is the fact that the percentage of chloric acid produced during photolysis of a solution of hypochlorous acid is identical with that given by chlorine water. Putting, for the sake of simplicity, the percentage of chloric acid given by 0·1*N*-solutions of both substances as 60 (actually 61), the stoicheiometric equations for the two photodecompositions are :

$$0{\cdot}05Cl_2 + 0{\cdot}05H_2O \longrightarrow 0{\cdot}01HClO_3 + 0{\cdot}09HCl + 0{\cdot}01O_2$$
$$0{\cdot}05HClO \longrightarrow 0{\cdot}01HClO_3 + 0{\cdot}04HCl + 0{\cdot}01O_2$$

equations which apparently hold whatever the degree of decomposition, and the former of which corresponds to that given by Popper for the decomposition of chlorine water. Thus a reduction of the final hydrochloric acid acidity by more than half makes no difference in the yield of chloric acid, while, on the other hand, if the final acidity is doubled by working with chlorine solutions with 0·1*N*-hydrochloric acid added, or suppressed by adding disodium hydrogen phosphate to hypochlorous acid solution, the chlorate percentage falls to about 30 or rises to more than 80, respectively.

Using the same value of the Jakowkin equilibrium constant and the same assumptions as previously, we have calculated the values of [HCl] in a number of solutions before insolation, half way through the insolation, and after complete decomposition. The results are contained in the following table.

Solution insolated.	[HCl] at start.	[HCl] after 50% decomp.	[HCl] at end.	Yield of chloric acid %.
0·05*M*-HClO + Na_2HPO_4	—	—	—	83
0·05*M*-HClO	—	0·013	0·04	61
0·05*M*-Cl_2	0·0225	0·0487	0·09	61
„ + 0·01*N*-HCl	0·0275	0·0575	0·10	55
„ + 0·1*N*-HCl	0·102	0·1455	0·19	29
„ + 0·5*N*-HCl	0·500	0·545	0·59	14

It is difficult at first sight to see why the solutions of 0·05*M*-hypochlorous acid and 0·05*M*-chlorine should give the same yield of chloric acid when the HCl acidity conditions are so different. We are inclined to attribute it to the fact that, as soon as decomposition of the hypochlorous acid has commenced, chlorine will be formed in the first layers of the cell. The solutions were not stirred during the experiments, owing to the volatility of the substances present. Consequently the first and absorbing layers will be different in composition from the solution in the rest of the cell, which is unaffected or only weakly affected by light. They will always contain more acid than the latter, and a high chlorine concentration in comparison with their hypochlorous acid content. Chlorine, moreover, absorbs far more strongly than hypochlorous acid. So that the solution is really being insolated under conditions which, both in respect of acidity and of nature of absorbing molecules, correspond far more closely to those in a chlorine-water solution than at first sight they appear to do. This seems a very possible explanation of the results observed.

With regard to the first stage of the reaction in these experiments, we have no doubt that both the hypochlorous acid and the chlorine

molecules are primarily photosensitive. All the experiments go to show this, and we cannot agree with the view expressed by Benrath and Schaffganz that the hypochlorite ion is the sole responsible photosensitive agent. Its concentration in 0·05*M*-hypochlorous acid is of the order of 2×10^{-5} and in 0·05*M*-chlorine about 10^{-8} equivalents/litre. Further experiments in this laboratory have shown that the quantum efficiency for the decomposition of a 0·06*N*-solution of sodium hypochlorite is about the same as for hypochlorous acid and for chlorine water, and we regard it as in the highest degree unlikely that this agreement would be obtained if, in all these solutions, the hypochlorite ion, with its widely different concentrations, were the sole photosensitive component.

Summary.

(1) The apparatus and experimental methods used in the investigation of the photodecomposition of chlorine water and hypochlorous acid solutions are described.

(2) It is shown that, except when substances are added which cause secondary reactions, the sole products of decomposition are hydrochloric and chloric acids and oxygen.

(3) Results are tabulated showing the percentage yield of chloric acid obtained in photolysis of chlorine water; chlorine water containing certain added acids, salts, etc.; hypochlorous acid; and hypochlorous acid containing added disodium hydrogen phosphate or sodium acetate.

(4) Secondary reactions were found with chlorine water containing manganese sulphate or cobalt sulphate (sometimes), and with mixtures of hypochlorous acid and sodium acetate.

(5) The results show that both the hypochlorous acid and the chlorine molecule are photosensitive, the latter possibly giving hypochlorous acid as a primary product. The evidence indicates that some at all events of the ions present in the salts used have a specific effect on the proportions of the products.

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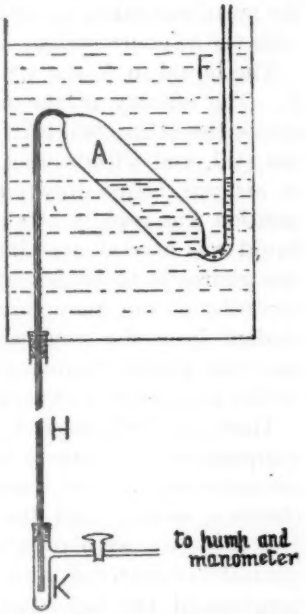
CXVIII.—*The Composition of the Liquid and Vapour Phases of Mixtures of Glycerol and Water.*

By MANATHATTAI PICHU IYER VENKATARAMA IYER and FRANCIS LAWRY USHER.

SINCE information about the loss of glycerol on evaporation of its concentrated solutions could not be found in the literature, we made the necessary measurements, and the results are now recorded.

Material.—The "chemically pure glycerine" (Merck) used contained no appreciable quantity of foreign substances, except water. A sample was distilled, and the first and the last fraction were free from volatile organic impurities and polyglycerols, respectively.

Method.—The proportion of glycerol in the vapour phase of mixtures of water and glycerol containing less than 75% of the latter is negligible. Solutions of high glycerol content rapidly change in composition when partly vaporised, and therefore the method of examination must involve not only the formation of as little vapour as possible, but also the rigorous prevention of any fractional condensation of it when once formed. A simple arrangement was used in which the possibility of such condensation was eliminated. The compositions of the liquid and of the condensed vapour were determined refractometrically.



A wide glass tube, A (see fig.), of about 300 c.c. capacity, which was used as the still, was sealed at its upper end to a length of thermometer tubing, H, and at its lower end to a tube, F, of about 5 mm. bore, through which the liquid was admitted or withdrawn. The still, set at an angle of 45°, was completely immersed in a large brine bath, the tubes F and H pointing vertically upwards and downwards, respectively. The latter, held by a cork in a tubulure in the floor of the bath, extended for about 50 cm. below the bath and passed through a rubber stopper fitting into a small receiver, K, which communicated, through a tapped side tube, with a Fleuss pump and a manometer.

About 180 c.c. of a glycerol-water mixture having been intro-

duced into A through the tube F, this was closed by stout rubber tubing carrying a screw-clamp, the apparatus was thoroughly exhausted through the side tube of K, and the tap closed. Burners placed outside the bath were regulated so that there was an upward temperature gradient from the bottom to the top (any condensation in the still thus being prevented). When a convenient quantity of liquid had collected in K—which always remained cold—the experiment was stopped by admitting air through F, and the condensate was immediately examined.

At the commencement and at the end of each experiment, a sample of the liquid in A was withdrawn by a pipette and analysed; the mean was taken as the composition of the mixture corresponding with the vapour condensed.

The liquid in A was stirred by admitting bubbles of air through F. The efficacy of the method was proved by introducing, one above the other, two mixtures of widely different composition into the still, and withdrawing successive samples while a slow stream of air was being drawn through the liquid; constancy of composition was rapidly attained. Owing to the slope of the still, no liquid was carried over into the capillary tube, and no error from this source is to be feared: indeed, the presence of a very small quantity of the main liquid in the condensate would be at once evident from the composition of the latter; but in nearly every case the points representing the composition of the vapour fell, within the limits of experimental error, on a regular curve.

Three methods suggest themselves for the determination of the composition of mixtures containing only glycerol and water: the measurement of the density, the estimation of the glycerol by chemical means, and the measurement of the refractive index. The first two were rejected as requiring an inconveniently large quantity of material, and the third was adopted. Since the temperature of the tap-water used for jacketing the prisms of the refractometer was 23—24°, the measurements were, for convenience, carried out at 25°. No trustworthy data for the refractive index of glycerol solutions at 25° are available, and the necessary measurements were therefore carried out. The density of the original sample of glycerol at 20° showed it to contain 97·75% of glycerol, and this liquid was used for the preparation of a series of solutions having a lower glycerol content, the dilution being carried out in dry stoppered bottles with known weights of water and the original solution. From time to time the compositions of these solutions were checked by density measurements. The solutions were examined in an Abbé (Hilger) refractometer at 25°, and a composition–refractive index curve was drawn. The transference of

samples of solutions of high glycerol content to the refractometer prism by means of a fine-pointed pipette did not occupy more than 2 or 3 seconds and no appreciable absorption of moisture could have occurred. The liquid, when once secured between the prisms, showed a constant refractive index for at least 10 minutes after it had attained the temperature of the water-jacket, whereas the time required to make the series of settings and readings (usually six) was less than 2 minutes. The sample of 100% glycerol was obtained by bubbling a stream of dry air through the 97·75% solution maintained at about 90°, until the refractive index attained a constant value.

Accuracy of the Results.—The accuracy of the results is affected mainly by one source of error, which is to some extent unavoidable in working with solutions of high glycerol content. Such solutions, yielding a vapour which consists largely of water, necessarily undergo on distillation a change in composition which is great compared with that attending the partial vaporisation of mixtures whose constituents have boiling points differing by a much smaller interval of temperature. This change in composition increases as the proportion of glycerol rises, and all that can be done to mitigate its effect on the accuracy of the results is (1) to vaporise as little of the liquid as possible, consistently with securing a fair sample, and (2) to take the mean of the compositions of the liquid before and after vaporisation. In any experiment in which a vapour phase is present, fractional condensation must occur in the receiver, but the error thus introduced may be neglected if the mass of vapour condensed is large compared with that remaining uncondensed. In our experiments this condition was secured by using a very small receiving system, the total volume of which was less than 20 c.c., whereas the amount of condensate varied from about 0·1 to 0·25 g., so that all but a fraction of 1% of the vapour was actually condensed, and the liquid so obtained could reasonably be considered a fair sample. Thirty-eight determinations were made, and a smooth curve was drawn through the points obtained by plotting the composition of the vapour against that of the liquid. A rapid change occurs in the composition of the vapour from solutions containing about 98% of glycerol, and therefore the curve had to be drawn through the experimental values for 98 and 99% glycerol. The value given for 99% glycerol may be as much as 2 or 3% in error, since the curve is very steep here, and no measurements could be made at higher concentrations; otherwise the maximum deviation of the experimental figures from those given by the curve is equivalent to 0·15% of glycerol. The following tables show (1) the corresponding percentages of glycerol by

weight in liquid and vapour for mixtures containing 75% of glycerol and more; and (2) the refractive indices of mixtures of glycerol and water at 25°.

	Percentage of glycerol in						
Liquid phase	75	80	85	86	87	88	89
Vapour phase	0·2	0·3	0·4	0·45	0·45	0·5	0·55
Liquid phase	90	91	92	93	94	95	96
Vapour phase	0·55	0·6	0·65	0·7	0·75	0·85	0·95
Liquid phase	97	98	99	100			
Vapour phase	1·2	1·7	17	100			

Refractive Indices.

Glycerol %	0	5	10	15	20	25	30
$n_D^{25°}$	1·3333	1·3394	1·3455	1·3516	1·3577	1·3641	1·3709
Glycerol %	35	40	45	50	55	60	65
$n_D^{25°}$	1·3777	1·3846	1·3917	1·3985	1·4058	1·4131	1·4204
Glycerol %	70	75	80	85	90	95	100
$n_D^{25°}$	1·4281	1·4357	1·4435	1·4506	1·4576	1·4651	1·4730

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CXIX.—*The Isomerism of the Oximes. Part XXI. Action of Picryl Chloride and of 2 : 4-Dinitrochlorobenzene on Aldoximes.*

By OSCAR L. BRADY and LOUIS KLEIN.

THE action of 2 : 4-dinitrochlorobenzene on a number of aldoximes was studied by one of us and Truszkowski (J., 1924, **125**, 1087); this work has now been extended to the action of picryl chloride, whilst an attempt has been made to elucidate some of the outstanding problems presented by the earlier work.

Dinitrochlorobenzene reacted with the sodium salts of *anti*-aldoximes in a somewhat similar manner to the alkyl halides, giving dinitrophenyl ethers, though these appeared to have the *syn*-configuration; these ethers, like the alkyl ethers, were difficult to hydrolyse with acid, but, whereas the alkyl ethers are stable to alkalis, the dinitrophenyl derivatives were readily decomposed giving the nitrile, thereby resembling the acyl derivatives of the *syn*-aldoximes. With the sodium salts of the *syn*-aldoximes, decomposition occurred with the formation of the aldehyde corresponding to the oxime but no nitrile. As was expected, picryl chloride behaved more like an acyl halide; with the sodium salts of *anti*-aldoximes it gave trinitrophenyl derivatives analogous to acyl derivatives, *e.g.*, the diphenylcarbamyl compounds (compare Brady and Dunn, J., 1913, **103**, 1613). These were fairly readily hydrolysed by concentrated hydrochloric acid to picric acid and

the carboxylic acid through the nitrile, or by alkalis to picric acid and the nitrile; if the customary convention is adopted, they must consequently be given the *syn*-configuration:

$$\begin{matrix} R\cdot CH \\ \| \\ N\cdot O\cdot C_6H_2(NO_2)_3 \end{matrix} \longrightarrow (NO_2)_3C_6H_2\cdot OH + R\cdot CN \longrightarrow R\cdot CO_2H.$$

The following picryl derivatives have been prepared from the sodium salts of the corresponding *anti*-aldoximes: picrylbenz*syn*-aldoxime, picryl-*o*-, *m*-, and *p*-nitro-, *o*- and *p*-methoxy-, 3 : 4-methylenedioxy-, *p*-dimethylaminobenz*syn*aldoximes, picrylcinnam-*syn*aldoxime, and picryl-4-picryloxy-3-methoxybenz*syn*aldoxime; no derivative could be obtained from the sodium salts of *o*- and *p*-hydroxybenz*anti*aldoximes.

With the sodium salts of *syn*-aldoximes a mixture of aldehyde and nitrile was obtained. The picryl chloride in this respect is intermediate in its action between dinitrochlorobenzene, which gives the aldehyde, and acetyl chloride, which gives the nitrile, but differs totally from the alkyl halides, which give stable *N*-alkyl compounds, from diphenylcarbamyl chloride, which gives diphenylcarbamyl derivatives of the *syn*-aldoximes (Brady and Dunn, *loc. cit.*), and from benzoyl chloride, which gives benzoyl derivatives of the *anti*-oximes (Brady and Thomas, J., 1922, **121**, 2104; Brady and Grayson, J., 1924, **125**, 1419; Brady and McHugh, unpublished work).

The mechanism of the reaction of 2 : 4-dinitrochlorobenzene on the sodium salts of the *syn*-aldoximes has been further studied (compare Brady and Truszkowski, *loc. cit.*). It seems most probable that an *N*-substituted derivative is first formed which is immediately hydrolysed to the aldehyde and β-dinitrophenylhydroxylamine, the latter unstable compound then decomposing (compare Borsche, *Ber.*, 1923, **56**, 1494):

$$\begin{matrix} R\cdot CH \\ \| \\ N\cdot ONa \end{matrix} + (NO_2)_2C_6H_3Cl \longrightarrow \begin{matrix} R\cdot CH \\ \| \\ (NO_2)_2C_6H_3\cdot N\cdot O \end{matrix} \longrightarrow R\cdot CHO + (NO_2)_2C_6H_3\cdot NH\cdot OH.$$

The method of decomposition of the β-dinitrophenylhydroxylamine could not be ascertained; the question is discussed in the experimental part (see p. 849).

Brady and Truszkowski (*loc. cit.*) found that 2 : 4-dinitrochlorobenzene gave the same addition compound with both *p*-methoxybenz*anti*- and *p*-methoxybenz*syn*-aldoxime. Owing to the instability of the latter oxime, it seemed possible that isomeric change occurred during the determination of the freezing points, particularly if a trace of hydrogen chloride were produced. The

fusion diagrams of 2 : 4-dinitrochlorobenzene with cinnam*anti*- and cinnam*syn*-aldoximes have been constructed. Although the latter *syn*-aldoxime is much more stable than *p*-methoxybenz*syn*aldoxime and its conversion to the *anti*-isomeride by traces of hydrogen chloride has not been observed, the same addition compound was obtained from both oximes. Moreover, rapid treatment with dilute sodium hydroxide broke up the addition compound into dinitrochlorobenzene and cinnam*anti*aldoxime; this seems to eliminate the possibility that the *anti*- is converted into the *syn*-aldoxime, a view previously entertained, since oximes which were known not to give *syn*-isomerides did not show compound formation with dinitrochlorobenzene.

EXPERIMENTAL.

Action of Picryl Chloride on anti-*Aldoximes.*—Benz*anti*aldoxime (12 g. = 1/10 mol.) was dissolved in warm alcohol (50 c.c.), a solution of sodium (2·3 g. = 1/10 mol.) in alcohol (50 c.c.) added, followed by a solution of picryl chloride (24·7 g. = 1/10 mol.) in warm alcohol (400 c.c.). A red colour developed and the picryl compound soon crystallised; after keeping for an hour, it was separated, and washed first with alcohol then with warm water, when a 70% yield of crude *picrylbenz*syn*aldoxime* was obtained. Crystallised three times from boiling acetone, it gave canary-yellow prisms, m. p. 181—182° (decomp.) (Found : N = 16·7. $C_{13}H_8O_7N_4$ requires N = 16·9%). Other picryl derivatives were prepared similarly from the corresponding *anti*-aldoximes.

The yields given are those of the crude products after washing and drying. The compounds were crystallised two or three times from boiling acetone unless otherwise stated : *Picryl*-p-*methoxybenz*syn*aldoxime* (yield 60%), sulphur-yellow needles, m. p. 142—143° (decomp.) (Found : N = 15·8. $C_{14}H_{10}O_8N_4$ requires N = 15·5%). *Picryl*-o-*methoxybenz*syn*aldoxime* (yield 100%), pale yellow prisms, m. p. 153—154° (decomp.) (Found : N = 15·9. $C_{14}H_{10}O_8N_4$ requires N = 15·5%). *Picryl*-3 : 4-*methylenedioxybenz*syn*aldoxime* (yield 80%), deep yellow, microscopic needles, m. p. 152° (decomp.) (Found : N = 15·0. $C_{14}H_8O_9N_4$ requires N = 14·9%). In the preparation of this compound more alcohol must be used in order to keep the sparingly soluble sodium salt of the oxime in solution. *Picryl*-o-*nitrobenz*syn*aldoxime* (yield 25%), pale yellow prisms, m. p. 157—158° (decomp.) (Found : N = 18·6. $C_{13}H_7O_9N_5$ requires N = 18·6%). This was more soluble than the other picryl derivatives and was crystallised from dilute acetone. The low yield was due to loss by solution in alcohol. *Picryl*-m-*nitrobenz*syn*aldoxime* (yield 80%), pale yellow cubes, m. p. 169° (decomp.) (Found : N = 18·7.

$C_{13}H_7O_9N_5$ requires N = 18·6%). *Picryl*-p-*nitrobenz*syn*aldoxime* (yield 60%), pale yellow prisms, m. p. 168° (decomp.) (Found: N=18·3. $C_{13}H_7O_9N_5$ requires N=18·6%). *Picryl*-p-*dimethylaminobenz*syn*aldoxime* (70% yield), orange-red prisms darkening at 110° and decomposing at about 130° (Found: N = 18·5. $C_{15}H_{13}O_7N_5$ requires N = 18·7%). This compound decomposes in hot acetone and cannot be crystallised satisfactorily from benzene, alcohol, chloroform, ether or acetic acid. It was purified by solution in cold acetone and cooling in ice, followed by the addition of water drop by drop with scratching until a suitable quantity had crystallised out. *Picrylcinnam*syn*aldoxime* (yield 65%), pale yellow prisms, m. p. 164—165° (decomp.) (Found: N = 16·1. $C_{15}H_{10}O_7N_4$ requires N = 15·7%). 3-Methoxy-4-hydroxybenz*anti*aldoxime (2·5 g. = 1 equiv.) was dissolved in alcohol (20 c.c.), and a solution of sodium (0·69 g. = 2 equiv.) in alcohol (20 c.c.) added; the mixture was cooled in ice, and treated with a solution of picryl chloride (7·4 g. = 2 equiv.) in alcohol (100 c.c.), the whole being then immediately cooled in ice. After some time, the precipitate was collected and washed as before (yield 34%). Using only one equivalent each of sodium and of picryl chloride, a much smaller yield of the same compound was obtained. From acetone solution on addition of water, *picryl-3-methoxy-4-picryloxybenz*syn*aldoxime* separated in very pale yellow prisms, m. p. 178—179° (decomp.) (Found: N = 16·8. $C_{20}H_{11}O_{15}N_7$ requires N = 16·6%). When a solution of the sodium salt of *o*- or *p*-hydroxybenz*anti*aldoxime was treated with picryl chloride, the only reaction which occurred was the decomposition of the picryl chloride, picric acid and the oxime being the only compounds recoverable even when 2 mols. of picryl chloride were employed (compare Brady and Truszkowski, *loc. cit.*).

*Alkaline Hydrolysis of Picrylbenz*syn*aldoximes.*—The method of hydrolysis employed varied considerably according to the nature of the product to be identified. In the cases of picryl-*o*-, *m*-, and *p*-nitrobenz*syn*aldoximes, the finely-powdered compound (2 g.) was suspended in 2*N*-sodium hydroxide (45 c.c.) for some time (ortho, 15 hours; meta, 6 hours; para, 48 hours) and the solution was then filtered. The solid residue was identified, after crystallisation if necessary, as the corresponding nitrile by the method of mixed melting points. The filtrate was shaken with concentrated potassium carbonate solution, the potassium picrate, which separated in characteristic silky needles, was decomposed with acid, and the picric acid identified. Picryl-3 : 4-methylenedioxybenz*syn*aldoxime (0·5 g.) was warmed for 3 minutes with 5% alcoholic sodium hydroxide (25 c.c.), diluted with water (50 c.c.), and left over-

night. The solid which had crystallised was identified as 3:4-methylenedioxybenzonitrile, and picric acid was identified in the solution. Picrylbenz*syn*aldoxime and picrylcinnam*syn*aldoxime were treated similarly, except that the liquid nitriles, obtained by extracting the diluted alcoholic solution with ether, were hydrolysed and the benzoic and cinnamic acids identified. Picryl-*p*-methoxybenz*syn*aldoxime (2 g.) was heated on the water-bath for 30 minutes with 2*N*-sodium hydroxide (35 c.c.), when a red solution was obtained and ammonia was evolved. Hydrochloric acid was added and, after cooling, the precipitate was collected and washed with cold water until the washings were no longer yellow. The residue was *p*-methoxybenzoic acid, and picric acid was isolated from the filtrate. *o*-Methoxybenzoic acid could not be separated from picric acid satisfactorily, so picryl-*o*-methoxybenz*syn*aldoxime (0·5 g.) was heated on the water-bath with 2*N*-sodium hydroxide (30 c.c.). Decomposition occurred slowly and oily drops appeared on the surface. The liquid was cooled and the oil removed with ether and subsequently hydrolysed with sodium hydroxide, when ammonia and *o*-methoxybenzoic acid were obtained, indicating that the oil was the nitrile. When picryl-*p*-dimethylaminobenz*syn*aldoxime was similarly treated, the oil solidified and was identified as *p*-dimethylaminobenzonitrile. Picryl-3-methoxy-4-picryloxybenz*syn*-aldoxime (0·5 g.) was heated for 2—3 minutes with 5% alcoholic potassium hydroxide, the solution diluted and saturated with carbon dioxide; after keeping over-night, potassium picrate separated, and chloroform extracted 3-methoxy-4-hydroxybenzonitrile from the solution.

*Acid Hydrolysis of Picrylbenz*syn*aldoximes.*—In the cases of picryl-*p*-methoxy-, 3:4-methylenedioxy-, and *p*-nitro-benz*syn*-aldoximes, the picryl compound was heated on the water-bath under reflux with concentrated hydrochloric acid for 6 hours. On cooling, picric acid and the corresponding benzoic acid crystallised out. The solid was washed with cold water until the washings were no longer yellow, and the residue identified as the corresponding benzoic acid. Very little *o*-nitrobenzoic acid was obtained owing to its solubility in water being similar to that of picric acid, whilst with picryl-*m*-nitrobenz*syn*aldoxime it was found impossible to separate satisfactorily the two acids produced. In the cases of picrylbenz*syn*aldoxime and picrylcinnam*syn*aldoxime, the acids were separated by steam distillation. When picryl-*o*-methoxybenz*syn*aldoxime was hydrolysed in this way, very little solid separated, so the solution was extracted with ether; the material thus removed, after crystallisation from water, was found to be salicylic acid, formed by the elimination of the methyl group

as methyl chloride. From the hydrolysis of picryl-*p*-dimethylaminobenz*syn*aldoxime only picric acid separated; this was removed and the filtrate made faintly alkaline with sodium hydroxide, when the cautious addition of dilute acetic acid precipitated *p*-dimethylaminobenzoic acid. Picryl-3-methoxy-4-picryloxybenz*syn*aldoxime could not be hydrolysed under the above conditions.

Action of Picryl Chloride on syn*Aldoximes.*—*p*-Methoxybenz*syn*aldoxime (2·5 g.) was dissolved by very gentle warming in alcohol (30 c.c.), and a solution of sodium ethoxide (0·38 g. of sodium in 10 c.c. of alcohol) added, followed by a warm solution of picryl chloride (4·13 g.) in alcohol (40 c.c.). An evanescent wine-red coloration developed changing to a dirty yellowish-brown with the deposition of a small amount of sodium chloride which was free from organic matter. The liquid after dilution was distilled in steam, the first portion passing over rich in alcohol being collected separately. From the second portion white crystals of *p*-methoxybenzonitrile separated; after drying in a vacuum, 0·8 g. was obtained corresponding to 36% yield. The filtrate from these was treated with semicarbazide hydrochloride and sodium acetate, whereupon, on stirring and keeping, *p*-methoxybenzaldehydesemicarbazone (0·66 g.) crystallised, identified by the method of mixed melting points. The alcoholic portion of the distillate gave no precipitate on dilution, but on treatment with semicarbazide hydrochloride and sodium acetate and concentrating gave a further 0·17 g. of the semicarbazone, making a total yield of 26% of aldehyde. Picric acid was isolated from the liquid in the distilling flask after removal of tar. Similar results were obtained using benz*syn*aldoxime, cinnam*syn*aldoxime, and hept*syn*aldoxime, except that in these cases the nitrile, being liquid at room temperature, did not separate. The whole of the distillate was accordingly treated with semicarbazide hydrochloride and sodium acetate, the semicarbazone separated, and the mother-liquor extracted with chloroform. After removing the solvent, the nitrile was hydrolysed with concentrated hydrochloric acid in the case of the benzonitrile, with 50% sulphuric acid in that of cinnamonitrile, and with 50% potassium hydroxide in the case of heptonitrile, and the acids were identified. The yield of aldehyde, weighed as semicarbazone, was: benzaldehyde 33%, cinnamaldehyde 28%, and heptaldehyde 24%.

Further Investigation of the Action of 2 : 4-*Dinitrochlorobenzene on* syn*Aldoximes* (Compare Brady and Truszkowski, *loc. cit.*).—The action of 2 : 4-dinitrochlorobenzene on *p*-methoxybenz*syn*aldoxime has been again investigated, but no indication of the formation of nitrile was obtained, thus confirming the earlier observation.

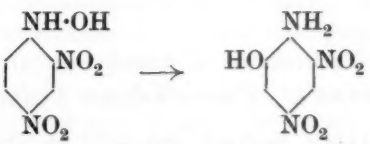
The action of 2 : 4-dinitrochlorobenzene on hept*syn*aldoxime has

also been investigated more fully, this compound being selected as a readily purified, stable *syn*aldoxime. A solution of 1·069 g. of sodium in 25 c.c. of absolute alcohol was mixed with one of 5·996 g. of hept*syn*aldoxime in 35 c.c. of absolute alcohol, and 9·412 g. of dinitrochlorobenzene in 35 c.c. of warm absolute alcohol were added. The mixture was left over-night in a corked flask, filtered, and the precipitate washed with a little absolute alcohol. The precipitate after drying in a vacuum over calcium chloride weighed 1·89 g.; it was dissolved in water and the brown solution made up to 100 c.c. A part was tested for hydroxylamine with negative results, whilst in another portion, acidified with nitric acid, the ionisable chlorine was determined by Volhard's method. The amount found indicated 59·4% chlorine in the solid, which apparently consisted of sodium chloride with a little highly-coloured impurity (NaCl contains 60·7% Cl). The filtrate from this solid was strongly acid to litmus. A portion was made strongly alkaline with sodium hydroxide to fix any unchanged oxime and extracted with chloroform to remove aldehyde, etc. The alkaline aqueous layer was treated with sufficient ammonium chloride to decompose the whole of the sodium hydroxide added and again extracted with chloroform, when a very small amount of hept*syn*aldoxime was obtained. The rest of the filtrate was distilled in steam to remove heptaldehyde. The liquid in the flask was heated with the addition of concentrated hydrochloric acid to induce if possible the hydrolysis of any β-dinitrophenylhydroxylamine, made alkaline with sodium hydroxide, and again distilled in steam; ammonia but not hydroxylamine could be detected in the distillate. The disappearance of the hydroxylamine does not seem to be due to the subsequent treatment of the mixture, since aldehyde is produced immediately (see action on acetaldoxime below), and it has been found that aldehyde cannot be distilled in steam even from a mixture of equimolecular quantities of heptaldehyde and hydroxylamine hydrochloride in water. Hydroxylamine can decompose according to the equation $3NH_2{\cdot}OH \longrightarrow NH_3 + N_2 + 3H_2O$, but it has been found that hydroxylamine can be distilled in steam practically quantitatively from an aqueous solution of hydroxylamine hydrochloride with two molecular proportions of sodium hydroxide. On the other hand, when 2 : 4-dinitrophenol, hydroxylamine hydrochloride, and excess of aqueous sodium hydroxide were distilled in steam, no hydroxylamine was obtained, but ammonia was detected, the amount being 92% of that demanded by the above equation. Under similar conditions, dinitrophenol and sodium hydroxide gave only a trace of ammonia. Dinitrophenol does not, however, decompose hept*syn*aldoxime in alkaline

solution. The difficulty in accepting the above method of decomposition of the hydroxylamine in the actual reaction is that no gas is evolved. As a result of these experiments, it seems that an *N*-dinitrophenyl derivative is first formed which immediately decomposes, the hydroxylamino-residue remaining attached to the dinitrophenyl radical; the β-dinitrophenylhydroxylamine then decomposes in such a way that no hydroxylamine is formed. An attempt was made to isolate these products of decomposition employing acet*syn*aldoxime, which has the advantage that the aldehyde formed is soluble in water. Acetaldoxime (12 g.) in alcohol (12 c.c.) was added to a solution of sodium (4·6 g.) in alcohol (100 c.c.), and a warm solution of 2 : 4-dinitrochlorobenzene (40·5 g.) in alcohol (150 c.c.) added. The liquid immediately turned dark brown and torrents of acetaldehyde were evolved. After cooling, the precipitate was found to consist of sodium chloride and some sodium dinitrophenoxide. On diluting the filtrate and leaving, a considerable amount of tar separated from which the only compound that could be isolated was a small quantity of dinitrochlorobenzene. From the mother-liquor small amounts of dinitrochlorobenzene and dinitrophenol were obtained. It seems, therefore, unlikely that the β-dinitrophenylhydroxylamine decomposed in the manner described for β-dinitrotolylhydroxylamine by Anschutz and Zimmermann (*Ber.*, 1915, **48**, 152),

$$3(NO_2)_2C_6H_2Me{\cdot}NH{\cdot}OH \longrightarrow (NO_2)_2C_6H_2Me{\cdot}NH_2 + (NO_2)_2C_6H_2Me{\cdot}N(O){\cdot}N{\cdot}C_6H_2Me(NO_2)_2 + 2H_2O,$$

as it should not have been difficult to isolate the sparingly soluble, high-melting amine or azoxy-compound. The alternative rearrangement



is unlikely and would not hold for the trinitro-compound. The only alternative therefore appears to be that the hydroxylamino-group is decomposed at the expense of the rest of the molecule, a view supported by the decomposition of hydroxylamine by dinitrophenol in the presence of alkali.

Fusion Diagram of the Cinnamaldoximes with 2 : 4-Dinitrochlorobenzene.

This was constructed in the usual manner, the freezing points being obtained from cooling curves. It was found impossible to

use a mixture containing more than 60% of the oxime owing to decomposition during melting. The results are given in Table I.

TABLE I.

Mol. % of cinnam*anti*ald-oxime.	F. p.	Eutectic.	Mol. % of cinnam*syn*ald-oxime.	F. p.	Eutectic.
0	48·8°		0	48·8°	
3·3	47·3		2·7	47·5	
6·4	49·8	47·1°	5·2	47·2	46·5°
19·4	60·5		7·6	46·8	46·8
21·6	62·6		9·9	48·8	46·6
25·7	64·2		21·6	61·0	
40·8	68·7		35·5	68·3	
50	69·6		45·2	69·2	
53·4	68·9		50	69·4	
57·9	67·5		52·4	69·3	
			58	68·1	

The maximum in each case (69·6°, 69·4°) corresponds to a compound of equimolecular quantities of dinitrochlorobenzene and the oxime, and in this neighbourhood the curves follow each other closely. When equimolecular quantities of each oxime and of dinitrochlorobenzene were melted together and the products mixed, the freezing point of this mixture was 69·6°. Each compound was ground for a few minutes with cold 2*N*-sodium hydroxide; the insoluble residue was dinitrochlorobenzene, whilst the solution on being saturated with carbon dioxide gave in each case cinnam*anti*aldoxime. There seems, therefore, little doubt that the two substances are identical.

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CXX.—*The Equilibria Underlying the Soap-boiling Processes. Pure Sodium Palmitate.*

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THE processes of soap boiling depend upon the existence of a series of well-defined equilibria, which have, however, received very little systematic study. The present contribution records observations upon equilibria in nearly two hundred systems containing pure sodium palmitate, water and sodium chloride over a range of temperature up to about 200° (in sealed tubes). Most of the work here recorded was completed in 1922 and the theoretical treatment in the previous communication by McBain and Burnett (J., 1922, **121**, 1320) was based upon a knowledge of these unpublished

results. Many of the systems were preserved and have now been re-examined together with fresh specimens. Their behaviour appears to be independent of time.

It is now possible to deal fairly simply with the various forms in which soap and its solutions occur. Probably every soap can be prepared in each of the two solid microcrystalline forms; namely, hexagonal plates and curd fibres. The hexagonal form may be dismissed for the present purpose, since it is only a transient, unstable form of sodium soap. The curd fibres contain water as well as traces of salt, and are characterised by their fineness. This involves a very large exposed surface, which makes it difficult to determine the relative amounts of chemically combined and sorbed water,* but it is certain that the hydration of the curd fibres depends upon the composition of the mother-liquor out of which they crystallised.

There are three forms of soap solution proper, all of them transparent, two are anisotropic or doubly refracting, and the third is isotropic, that is, dark when examined between crossed Nicols. These three forms of transparent solutions will be referred to as "neat soap," "middle soap," and "isotropic solution." All these are separate phases, mutually immiscible. Dr. K. Maclennan of Port Sunlight (*J. Soc. Chem. Ind.*, 1923, **42**, 3937) has rendered valuable service in directing attention to the importance of anisotropic plastic liquids in the soap-boiling processes. We find that every soap solution in sufficiently high concentration is anisotropic (doubly refracting, "liquid crystal," "mesomorphic"). This property is not confined to any one concentration, but extends over a wide range of composition even to concentrated soap solutions containing a certain amount of salt.

These remarkable solutions are clear, transparent, plastic masses which readily flow under their own weight when prepared in quantity as in the soap pan. Small specimens retain their shape indefinitely and look like pieces of clear, stiff jelly, from which, however, they differ fundamentally. A jelly is highly elastic and when not under strain is isotropic, whereas these anisotropic liquids are always doubly refracting and are largely devoid of elasticity. For instance, if a small portion of the surface of a specimen of $3N_w$(weight normal)-potassium laurate is pulled up into a sharp point with a glass rod, the projecting tongue retains its form and position apparently unchanged even after 10 years, but if jarred, assumes new positions under the stress and, if again undisturbed, retains these new forms indefinitely. In other words, the flow is plastic, not elastic or

* For previous communications on this subject, see J., 1919, **115**, 1300; 1921, **119**, 1369, 1669, 1374; 1924, **125**, 1971.

viscous, and there is no relaxation under a small force applied for a long time.

We have established that anisotropic and isotropic soap solutions constitute separate immiscible phases. Dissolution of the clear plastic anisotropic liquid in water requires time even with vigorous stirring. Their separate existence in different ranges of concentrations and their immiscibility has been substantiated in this laboratory by W. J. Elford for potassium laurate, by F. Maggs for potassium oleate, by H. M. Kamil for sodium abietate, by D. P. Davies for sodium ricinoleate, and by Miss E. M. Grant for potassium laurate at high temperatures (all unpublished).

One of the two anisotropic forms, " neat soap," is familiar to all soap-boilers, because most good household soaps are derived from it. It is a homogeneous, plastic liquid at the boiling point which forms the upper layer in the soap pan or kettle in the fitting, settling, or pitching process and it is characterised in industry by its content of about 63% of fatty acid for sodium soaps and about 40% of fatty acid for potassium soaps. The commercial neat soap, however, is but one particular case, and we have followed the continuous field of existence of this phase back to pure aqueous solutions of the salt of one fatty acid and up to pure molten anhydrous sodium soap.

The existence of the other anisotropic soap which occurs in medium concentrations and which we therefore call " middle soap " has been hitherto unsuspected, although it will become evident from the position of its field of existence that it may play an important and disturbing *rôle* both in the manufacture and in the use of soap preparations. It appears to be a conic anistropic liquid (McBain, *Nature*, 1924, **114**, 49; see there photograph by W. J. Elford).

The boundary between " middle soap " and " neat soap " has not yet been sufficiently elucidated owing to experimental difficulties which are only now being overcome. It is certain that they are separate, immiscible phases at higher temperatures, and it is probable that they remain so even at the lowest temperatures.

There is a wide range of soap solutions, with and without added salt, all of which are isotropic, not lighting up the field between crossed Nicols. This range extends continuously from pure water up to a definite limiting concentration of soap, which limit is even higher when salt is added. Within this continuous field the viscosity and other properties of the soap solutions vary greatly, and in the parts of the field representing the higher concentrations of soap, and those to which an optimum amount of salt has been added, the solutions often assume the form of true elastic transparent jellies which are, of course, isotropic. The part of this field where the solutions contain much salt and but little soap includes the

thin "lyes" of the soap pan or kettle, whereas the solutions containing more soap and a fairly large amount of salt include the "nigre" * the separation of which from the "neat soap" layer constitutes the final stage of the soap-boiling processes. These isotropic soap solutions cover an extremely wide range at very high temperatures. Above 316°, for example, sodium palmitate is an isotropic liquid miscible in all proportions with water or salt solutions.

This simple formulation of the possible forms in which soap may appear, which has required so many years of study for its elucidation, reduces the experimental problem merely to a determination of the limiting concentrations which bound the isotropic and anisotropic fields, respectively. The variations in the third possible phase—the curd fibres—are relatively small, although they merit further detailed investigation, because these fibres are the main constituent of household soap.

The present paper, then, consists essentially of a delimitation of the ranges of concentration of the two forms of soap solution together with an indication of the phases which can co-exist in equilibrium. The results are of general significance, for all the typical equilibria of the soap-boiling processes (silicates apart) are to be found in soap systems prepared from a single fatty acid. Furthermore, all sodium and potassium soaps, pure or commercial, exhibit the same type of equilibria, differing only in the exact concentrations at which the various phases appear.

Experimental.

Method.—The method of examination has been partly described in the previous communication with Burnett. It rests upon the principle that supersaturation does not occur in regard to the appearance of a liquid phase, a direct deduction from the kinetic theory.† It is our experience that this is likewise true of both forms of the anisotropic liquid—which distinguishes them significantly from crystalline phases. On cooling the homogeneous solution to its critical temperature, droplets of anisotropic liquid promptly appear, and on rewarming with efficient stirring the emulsion becomes homogeneous at exactly the same temperature. The phenomenon is thus independent of time or of the direction from which it is approached, provided that the stirring is really efficient.

* So-called because colouring matters go into this layer, making it dark brown.

† Crystallisation to form curd fibres, on the contrary, usually occurs only after at least four or five degrees of undercooling.

This visual observation is confirmed and rendered much more precise by examination between crossed Nicols whenever the liquid appearing or disappearing is anisotropic. The temperature at which the contents of the sealed tube become completely isotropic and dark between crossed Nicols is the same as the temperature at which the mixture becomes homogeneous on warming and stirring.* As the temperature is lowered, the degree of anisotropy is observed to increase, but it is impossible to follow quantitatively the extent to which isotropic liquid is replaced by anisotropic liquid with this form of examination in a large sealed tube immersed in a thermostat at high temperature, or to determine the temperature at which the transformation is complete. This is only possible with a thin section under a microscope using a solution appreciably below its boiling point. None of these solutions boils at a temperature more than a few degrees above 100°, but they can be studied in sealed tubes up to a temperature of several hundred degrees.

Determination of the solubility of curd fibres of soap resolves itself into an observation of the temperature at which, with efficient stirring, the last curd fibre just dissolves. A useful check in determinations with very cloudy concentrated solutions is suddenly to chill the specimen when the curd is thought to have melted; a pronounced change in appearance shows that curd had dissolved. This test is very distinct and defines the " melting point " within a degree. For the systems to be discussed in the present paper, sodium palmitate at room temperature is nearly insoluble and addition of salt reduces its solubility still further, so that all systems consist of opaque, white masses of crystalline curd fibres of hydrated soap enmeshing the remaining liquid which is practically devoid of soap (see, for example, Laing and McBain, J., 1920, **117**, 1525). The equilibrium or phase-rule diagram at room temperature consists of a short line at the top representing composition of the curd fibres and a long line at the bottom representing aqueous salt solutions containing traces of sodium palmitate. The only possible systems at room temperature are mixtures of curd fibres with this salt lye in various proportions.

With rise of temperature, the solubility of the curd fibres increases enormously so that a $1{\cdot}0N_w$-solution of soap is in completely homogeneous solution at 67°. The general form of these equilibria and the effect of salt can be deduced from the data for sodium laurate in the previous communication. The present paper is concerned with the equilibria at high temperatures, and all that it is necessary to remember is that below about 70° the anisotropic liquid com-

* If stirring is avoided the layers with a mirror-like surface are preserved up to temperatures far above the critical.

pletely disappears owing to the formation of curd fibres. It is easy, however, to get a suspended transformation at much lower temperatures.

Materials.—It is difficult to obtain large samples of sodium palmitate of sufficient purity to lend themselves to the present purpose. Most commercially pure sodium palmitates yield deep brown solutions; although if pure, even highly concentrated solutions should be colourless. On keeping at 150° for a day or two, concentrated solutions gradually darken. For the preliminary work, specially that dealing with low concentrations and equilibria between nigre and lye, a specially made specimen of English origin was used, although from analysis it contained some stearate. The later work was carried out with two specimens made by Kahlbaum, although neither of these was nearly as good, either in neutrality or colour, as solutions made by ourselves from sodium drippings and palmitic acid "Kahlbaum." The first Kahlbaum specimen was distinctly alkaline, 1 g. containing 0·0012 g. of sodium hydroxide (*i.e.*, 0·9 equivalent % excess of alkali). This is almost enough to salt out the soap in very highly concentrated solution. Kahlbaum's second specimen was nearly neutral, containing only 0·1 equivalent % excess of alkali. This was used for nearly all experiments in high concentration. To harmonise the results given by the first specimen for temperatures of appearance of two liquid layers with those obtained with the Kahlbaum material, 40° was subtracted from the former observations and the data recorded include this correction. It may be recalled that the colour accumulates in the nigre, the anisotropic "neat soap" being very much paler.

The solutions were made up in sealed evacuated tubes with boiled-out, distilled water. "A.R." or "Kahlbaum's purest sodium chloride" was used. Owing to the extreme viscosity or plasticity of the materials, the contents of a number of the tubes never became thoroughly mixed and such experiments were discarded. Concentrations are expressed in weight normality (gram-equivalents per kilo. of water); in "fractions" (1 gram-equivalent of sodium palmitate, 1 gram-equivalent of salt, and 1 kilo. of water, each being taken as unity; thus a solution which is weight normal with regard to sodium palmitate as well as to salt is 0·333 sodium palmitate, 0·333 salt, and 0·333 water); and in technical units, namely, percentage of fatty acid and of salt in 100 parts of water by weight of the mixture (thus the solution just described is 19·2% fatty acid and 4·4% salt).

Applicability of the Phase Rule.

It is our experience that the properties of a soap solution are completely determined by its composition and temperature, and

it is evident that the equilibria within the solution are defined to within about 1%. In the previous communication, the view was advanced that from the standpoint of the phase rule such a colloidal solution behaves as a single phase towards external equilibria with other phases. This suggestion that the phase rule is directly applicable is borne out by all our observations; in fact, only eight tubes out of nearly a thousand studied have suggested even a slightly discrepant behaviour; these will be discussed later. Even if these slight divergences are substantiated, the phase rule constitutes an excellent description of the equilibria involving soap solutions and the soap-boiling processes. Indeed, the equilibria in soaps of mixed commercial oils and fats (apart from the formation of curd) closely resemble those of a three-component system such as that derived from a single pure soap, a single salt and water.

In the three-component system sodium palmitate–sodium chloride–water there is one degree of freedom if, in addition to vapour, two other phases are present, and the temperature is fixed. That is to say, if both phases can vary in composition, they must do so in dependence upon each other, and it is only when three phases are present in addition to vapour that the compositions of those phases are completely fixed for any definite temperature. At a given temperature, such as the boiling point, the commonly occurring equilibria involve two liquids, or a liquid and a solid (curd fibres). In the soap pan, the usual equilibria are (*a*) anisotropic liquid, "neat soap," with isotropic liquid, "nigre," (*b*) anisotropic liquid soap with isotropic liquid lye, and (*c*) the more complicated equilibria involved in graining out, where, in addition to anisotropic liquid soap and liquid lye, curd fibres of the soaps of the more insoluble fatty acids progressively separate out. In soap-boiling practice, owing to the mixture of highly soluble with the more insoluble soaps, there is never sufficient salt added completely to grain out the whole of these soaps as curd fibres.* Equilibria between (*d*) isotropic nigre and isotropic lye occur in solutions much too dilute to appear in the soap pan; and the equilibria between (*e*) an isotropic soap and curd fibres in the absence of lye occur only in concentrations above those used in the soap pan, but they occur when neat soap is cooled in the frames.

Analysis of the Separate Layers.—Systems in which three liquid layers occur should exist at only one temperature whenever the total composition of the system is fixed. However, eight instances were met with in which three layers seemed to persist over a range of temperatures of 10° to 40°. The three layers involved were neat soap, nigre and lye. The total composition of the system approxi-

* This point was not made clear in the Fourth Colloid Report.

mated in each case to that of nigre. This slight, but distinct deviation from the requirements of the phase rule is not due to hydrolysis, but might well be due to a lag in the establishment of the internal equilibria. It is certainly due in part to the difficulty of thoroughly mixing and then separating the most viscous layer. In any case, 30° is only a small fraction of the range of temperature over which the equilibria have been studied and the phenomenon is confined to one small part of the diagram, namely, that where the nigre contains its maximum amount of salt. It was met with, for example, in tubes in which the sodium palmitate was 0·605, 0·608, 1·009, and $0{\cdot}383N_w$, respectively, and the sodium chloride 1·440, 1·30, 1·465, and $1{\cdot}504N_w$, respectively. The second instance is particularly interesting, as it apparently occurs at the exact point at which, on heating at 141°, three layers are converted into one homogeneous layer and the discrepancy in all cases consists in the persistence of the middle layer at temperatures appreciably below this. Thörl and Bätz (see later) obtained three layers in most of their experiments, but they worked at a constant temperature and the composition of each of their three phases was constant almost within the error of experiment.

Table I contains the results of analyses of the separate layers of a few tubes, the first four of which exhibited the persistence of three layers over a temperature range of about 30°. All the analyses show the high degree of entanglement of the middle layer in the plastic upper layer of neat soap, and the analysis of the middle layer in the first tube showed that it included large amounts of the upper layer. The lye contains only negligible amounts of sodium palmitate and separates completely from nigre. Before analysis, the tube containing the system was heated with occasional shaking at 90° for several days, then suddenly chilled, and opened for analysis. Water was calculated by difference.

TABLE I.

Weight normalities (N_w) of soap and salt in liquid phases co-existing at 90°.

	Neat soap.		Nigre.		Lye.	Total system.	
No.	NaP.	NaCl.	NaP.	NaCl.	NaCl.	NaP.	NaCl.
1	3·45	0·89	2·41	1·01	0·96	1·40	0·93
2	2·91	0·83	0·65	1·11	1·06	1·42	0·89
3	2·88	0·73	0·54	1·15	0·99	1·30	0·94
4	2·94	0·75	0·61	1·10	1·08	1·18	0·93
5	3·83	0·57	2·80	0·63	—	2·87	0·48
6	3·33	0·66	1·56	0·71	—	2·49	0·55
7	3·36	0·87	0·85	0·90	—	1·50	0·83
8	2·53	0·91	—	—	1·17	0·606	1·15
9	—	—	0·377	0·98	1·02	0·296	0·98

Table II.

Solubility of curd fibres of sodium palmitate as shown by the minimum temperature (T) at which they just completely dissolve to form one homogeneous liquid.

Sodium palmitate.			Sodium chloride.			
N_w.	Fraction.	% F.A.	N_w.	Fraction.	% salt.	T.
10·0 (K)	0·9091	65·3	—	—	—	(90°)
1·009	0·5022	19·5	—	—	—	67
0·504	0·3354	10·9	—	—	—	63
3·018	0·6998	40·1	0·2935	0·0682	0·92	(77)
1·008	0·3745	18·8	0·680	0·2531	3·01	76
0·5044	0·2194	10·5	0·7943	0·3455	3·91	74*
0·504	0·2457	10·6	0·55	0·2668	2·74	72
0·504	0·2348	10·6	0·642	0·2991	3·19	76
0·503	0·2245	10·5	0·738	0·3295	3·65	75·5
0·3987 (K)	0·1730	8·5	0·9065	0·3933	4·55	76
0·3515	0·1608	7·5	0·8347	0·3818	4·46	75
0·2063	0·1010	6·0	0·8358	0·4094	4·35	74
0·1353	0·0692	3·1	0·8189	0·4191	4·41	72·5
0·06096	0·0326	1·4	0·8067	0·4319	4·43	72·5
0·0583	0·0297	1·3	0·9082	0·4618	4·97	(75)

K = Kahlbaum's sodium palmitate.

* On undercooling, two layers formed at about 30°.

Table III.

Temperatures (T) at which, upon cooling, a single liquid soap solution separates into two liquid layers both isotropic (nigre and lye).

Sodium palmitate.			Sodium chloride.			
N_w.	Fraction.	% F.A.	N_w.	Fraction.	% salt.	T.
1·297	0·4009	22·7	0·9396	0·2903	3·88	98°
1·180	0·3793	21·1	0·9303	0·2991	3·93	92·5
1·000	0·3335	18·5	0·9984	0·3330	4·37	98
0·8610	0·3006	16·4	1·003	0·3501	4·51	88
0·7776	0·2799	15·1	1·001	0·3601	4·59	92
0·6947	0·2502	13·7	1·081	0·3896	5·03	95
0·6061	0·2196	12·2	1·155	0·4185	5·46	119
0·5669	0·1968	11·4	1·277	0·4490	6·06	145
0·5659	0·2203	11·5	1·003	0·3904	4·82	80
0·5425	0·2005	11·0	1·163	0·4299	5·58	115
0·4944	0·1950	10·2	1·042	0·4110	5·08	84
0·4613	0·1782	9·5	1·127	0·4353	5·51	85
0·4455	0·1797	9·3	1·034	0·4170	5·10	78
0·4180	0·1601	8·7	1·194	0·4572	5·89	125
0·3810	0·1604	8·1	0·9942	0·4187	4·99	84
0·3405	0·1376	7·2	1·133	0·4580	5·70	121
0·2960	0·1300	6·5	0·9797	0·4303	5·02	90
0·2842	0·1287	6·2	0·9234	0·4184	4·77	60
0·2782	0·1193	6·1	1·052	0·4516	6·40	123
0·2018	0·0907	4·4	1·022	0·4594	5·35	95·5
0·1981	0·0889	4·4	1·029	0·4620	5·40	88
0·1054	0·0502	2·4	0·9883	0·474	5·32 above	143
0·1001	0·0502	2·4	0·8930	0·4480	4·83	94
0·0997	0·0502	2·6	0·8851	0·4459	4·79	71
0·0279	0·0143	0·7	0·9317	0·4753	5·12	85
0·0202	0·0098	0·5	1·046	0·5060	6·11	141

Table IV.

Temperatures (T) at which, upon cooling, a single isotropic liquid soap solution separates into two liquid layers, isotropic nigre and anisotropic neat soap.

Sodium palmitate.			Sodium chloride.			
N_w.	Fraction.	% F.A.	N_w.	Fraction.	% salt.	T.
6·58	0·8506	57·2	0·154	0·0199	0·32	above 155°
5·46	0·8198	53·3	0·1995	0·0300	0·46	,, 160
4·87	0·7632	50·5	0·514	0·0804	1·26	,, 161
4·135	0·7394	46·9	0·4583	0·0820	1·23	,, (153)
4·131	0·7401	46·9	0·4523	0·0810	1·21	,, (160)
4·054	0·7782	46·1	0·1562	0·0300	0·43	(150)
3·975	0·7911	46·6	0·0497	0·0099	0·14	above 150
3·508	0·6993	43·2	0·5084	0·1014	1·48	,, (155)
3·389	0·7492	42·1	0·1348	0·0298	0·40	143
3·284	0·7396	42·1	0·1558	0·0351	0·47	81
3·185	0·7303	42·4	0·1775	0·041	0·55	74
3·126	0·7199	41·0	0·2158	0·0497	0·67	78
3·082	0·7169	40·6	0·2175	0·0506	0·68	80
2·976	0·6987	39·8	0·2775	0·0652	0·88	86
2·871	0·6594	38·9	0·4833	0·1110	1·55	above 158
2·818	0·7088	38·8	0·2040	0·0507	0·66	62
2·808	0·6634	38·9	0·4250	0·1004	1·36	145
2·702	0·6784	37·7	0·2805	0·0704	0·93	70
2·700	0·6717	37·7	0·3223	0·0801	1·06	76
2·653	0·6615	37·2	0·3572	0·0891	1·20	82
2·586	0·6492	36·7	0·3997	0·1001	1·34	85
2·486	0·6167	35·7	0·5459	0·1354	1·85	127
2·007	0·5423	31·0	0·694	0·1875	2·54	82·5
2·007	0·5594	31·1	0·5801	0·1617	2·13	46
1·958	0·5495	30·6	0·6049	0·1698	2·24	86
1·500	0·4502	25·3	0·8305	0·2494	3·31	92·5
1·492	0·4550	25·2	0·7875	0·2401	3·15	61
1·464	0·4480	24·9	0·8064	0·2461	3·21	61
1·417	0·4285	26·0	0·8900	0·2692	3·60	95·5
1·403	0·4207	24·0	0·9326	0·2796	3·37	104
1·374	0·4505	23·8	0·6758	0·2215	2·78	41
1·297	0·4009	22·7	0·9396	0·2903	3·88	98
1·290	0·4002	22·5	0·9333	0·2896	3·86	80
1·214	0·3954	21·6	0·859	0·2796	3·62	57
1·180	0·3793	21·1	0·9303	0·2991	3·93	92·5
1·03	0·3387	18·8	1·013	0·3328	4·40	88·5
1·021	0·3583	18·9	0·829	0·2908	3·64	46
1·014	0·3523	18·8	0·865	0·3005	3·80	49
1·009	0·3271	18·5	1·075	0·3485	4·68	91
1·001	0·3649	18·7	0·742	0·2705	3·28	37
0·7415	0·2655	14·4	1·042	0·3744	4·80	86
0·7409	0·2694	14·2	1·008	0·3667	4·66	54
0·6682	0·2598	13·3	0·9033	0·3513	4·26	41
0·666	0·3298	13·4	0·760	0·2894	3·61	32
0·6634	0·2353	13·1	1·157	0·4102	5·40	95
0·6582	0·2324	13·0	1·174	0·4145	5·50	98
0·608*	0·2084	12·1	1·30	0·4485	6·10	141
0·5456	0·2017	11·0	1·160	0·4285	5·56	91·5
0·503	0·2003	10·2	1·008	0·4015	4·90	64
0·503	0·2116	10·4	0·874	0·4207	4·29	37

* Formed three layers, two disappearing at about the same temperature.

TABLE V.

Temperatures (T) at which, upon cooling, a single liquid soap solution separates into two liquid layers, one isotropic and the other anisotropic ("middle soap").

Sodium palmitate.			Sodium chloride.			
N_w.	Fraction.	% F.A.	N_w.	Fraction.	% salt.	T.
0·2952	0·7469	40·0	—	—	—	155°
1·991	0·6657	31·6	—	—	—	141
1·683	0·6273	28·4	—	—	—	123
1·454	0·593	25·6	—	—	—	97
1·363	0·5768	24·4	—	—	—	87
1·277	0·5610	23·2	—	—	—	80
1·009	0·5022	19·5	—	—	—	65
3·389	0·7492	42·9	0·1348	0·0298	0·40	143
3·284	0·7396	42·1	0·1558	0·0351	0·47	81
3·263	0·7510	42·1	0·0872	0·0200	0·26	130
2·855	0·7188	39·2	0·1184	0·0298	0·44	140
2·843	0·7101	39·1	0·1618	0·0404	0·53	119
2·818	0·7088	38·8	0·2040	0·0507	0·66	62
2·811	0·7006	38·7	0·2020	0·0503	0·66	66
2·777	0·6911	38·4	0·242	0·0604	0·79	above 63
2·771	0·6908	38·3	0·2414	0·0602	0·79	80
2·513	0·6797	36·3	0·1841	0·0498	0·63	122
2·435	0·6600	35·5	0·256	0·0694	0·88	66
2·356	0·6598	34·9	0·2135	0·0598	0·75	103
2·235	0·6694	34·0	0·1024	0·0306	0·37	146
2·191	0·6412	33·4	0·2252	0·0660	0·81	93
2·150	0·6489	33·0	0·1645	0·0497	0·60	125
1·868	0·6190	30·2	0·1508	0·0500	0·57	121
1·728	0·6088	28·7	0·1104	0·0389	0·44	106
1·561	0·5974	26·8	0·0525	0·0201	0·21	98

Experimental Data.—Temperatures at which curd fibres completely dissolved to form homogeneous liquid or anisotropic liquid are collected in the last column of Table II. The composition recorded is the solubility of sodium palmitate at that temperature and it is seen that the solubility depends upon the amount of salt present. The first three columns give the concentration of sodium palmitate and the second three of sodium chloride in weight normalities, modified molar "fractions," and technical units, respectively. In the two cases indicated, where the formation of curd on cooling was suspended, two liquid layers were formed at a lower temperature. Two degrees have been subtracted from the results obtained with sodium palmitate other than Kahlbaum.

In Table III are collected the observations upon systems which are homogeneous, isotropic liquids at high temperatures and, on cooling, separate into two liquid layers both of which are isotropic (nigre and lye).

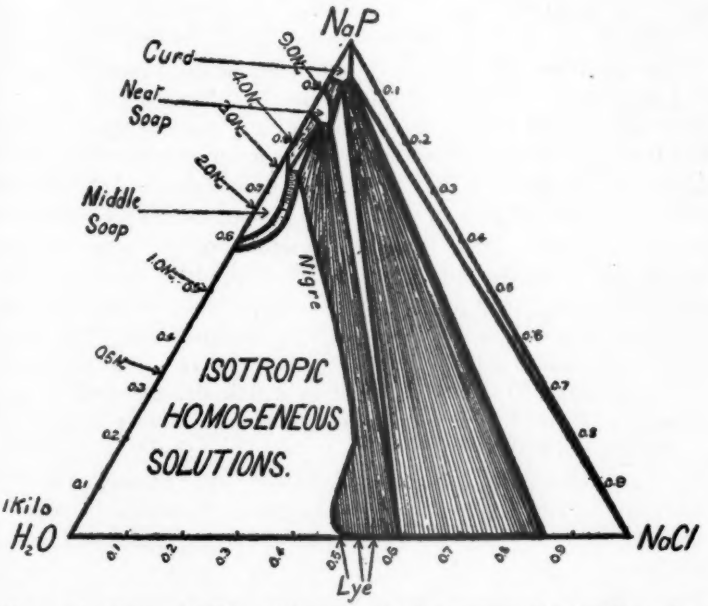
In Table IV are collected the observations upon solutions which at very high temperatures are homogeneous and isotropic but which on cooling separate into two liquid layers, one isotropic and the

other anisotropic. These pairs correspond to the soap boiler's nigre and neat soap, respectively. In many instances, owing to the consistency of the plastic liquid, the two phases did not separate into two distinct layers but remained coarsely emulsified.

Discussion of Results.

The work carried out in this laboratory clearly establishes for the first time the general properties of the whole of the phase-rule diagram for soaps with and without salt. Many quantitative

FIG. 1.



Phase rule diagram at 90°, concentrations being expressed in fractions of mols. of sodium palmitate and sodium chloride, but in fractions of one kilogram for water. The shaded areas represent the approximate direction of the tie lines in the two-layer systems.

measurements remain to be carried out, but the largest part of the diagram, that involving isotropic solutions, has been accurately mapped and the nature and the approximate composition of the phases in equilibrium with them have been determined. The results are best discussed with reference to the accompanying diagrams.

Fig. 1 represents the equilibria and stable phases at 90°. It is the same equilateral triangle of unit height used in the previous paper by McBain and Burnett, in which the respective corners represent 1 mol. of pure anhydrous sodium palmitate, 1 mol. of sodium chloride, and 1 kilo. of water; and in which the co-ordinates

are the fractions of these three quantities the sum of which for each point on the diagram is unity. Although this is not so easily read as the rectangular diagram given below, it is much more satisfactory for a complete survey of the field.

Nearly half the diagram is occupied by the field of isotropic solutions beginning with pure water and remaining single homogeneous liquids when soap and salt are added up to rather high concentrations. The internal equilibria of these solutions, which range from crystalloidal to wholly colloidal, are discussed in other communications. (It may be mentioned, however, that "middle soap," like isotropic soap, is a colloidal electrolyte.) The isotropic field extends up to saturated aqueous solutions of sodium chloride.

There are three other fields representing single phases of varying composition; namely, curd fibres (at the top of the diagram), anisotropic "neat soap," and anisotropic "middle soap." There is but one phase of constant composition, namely, crystalline sodium chloride, which is found at the lower right hand point of the diagram.

There are seven fields in which two phases each of varying composition co-exist; namely, (A) "middle soap" and isotropic solution, (B) "middle soap" and "neat soap," (C) "neat soap" and curd fibres, (D) "neat soap" and isotropic solution (which latter in this region is called "nigre" by soap boilers), (E) "neat soap" and isotropic solution (which is always called "lye"), at the bottom of the diagram, (F) a small region in which the isotropic solution separates into two layers corresponding approximately to nigre and lye, and (G) curd fibres and lye up to its saturation point with salt. Whenever three phases co-exist at barometric pressure, each is of fixed composition, as shown by the diagram. Solid sodium chloride cannot exist in contact with any phase except saturated lye and curd fibres.

The chief fields occurring during soap-boiling processes are (D) (during fitting), (E) (when rather more salt has been added but not enough to salt or grain out); but it is only when the neat soap is cooling in the frames that (C) is met with through the separation of curd fibres, at much lower temperatures.

The forms of the fields for neat soap and for curd fibres are only approximately known, but the general position is fixed by an accurate knowledge of one or two points in each.

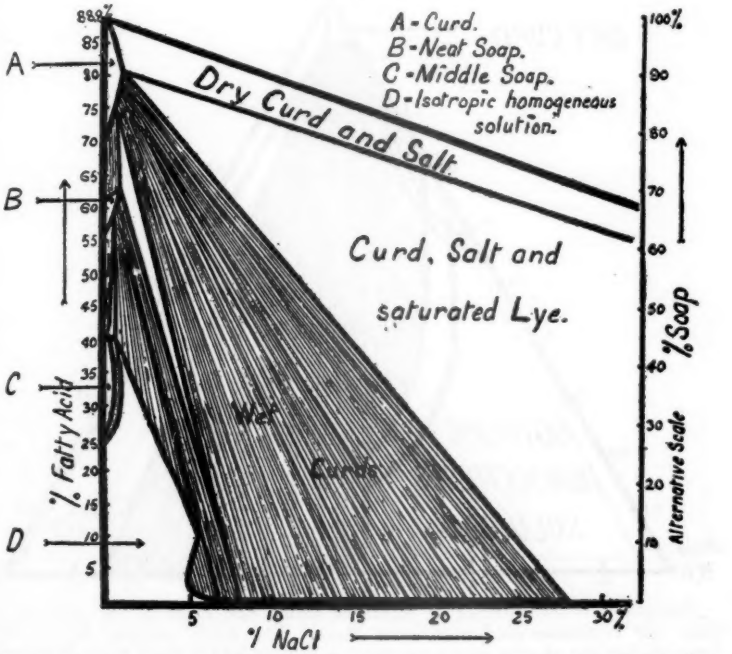
Fig. 2 is similar to Fig. 1, but is very much more easily read, since rectangular co-ordinates are used. For convenience of comparison with soap-boiling data, technical units are employed.* The diagram

* This possibility of direct comparison is specially important, since in ordinary soap boiling glycerol also is present and it is seldom that a complete analysis of each phase is available.

refers to 100°. It will be observed that the tie lines are straight; in other words, as on the triangular diagram, any point in a heterogeneous field quantitatively represents the respective amounts of the two phases lying at the ends of the straight tie line passing through that point.

Fig. 3 represents the effect of cooling solutions to a lower temperature, such as 68°, at which the curd fibre of sodium palmitate is so much less soluble that no soap solutions concentrated enough

FIG. 2.



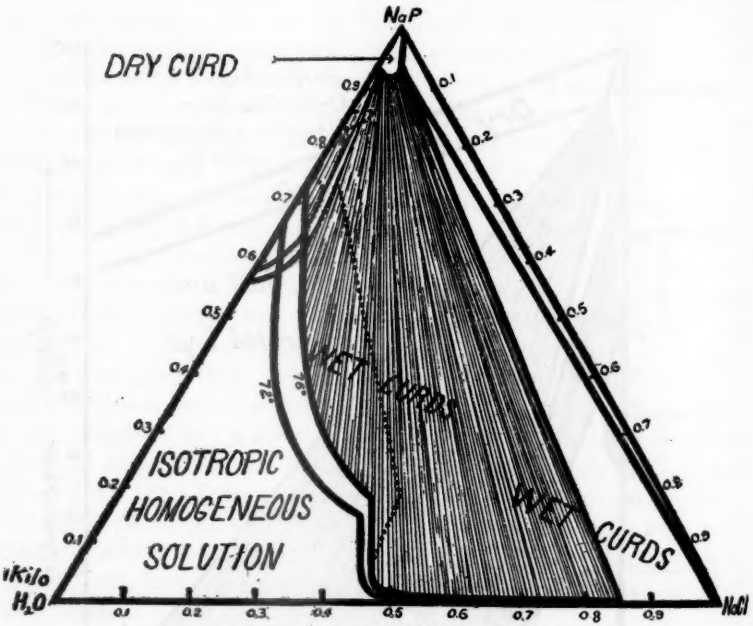
Phase rule diagram at 100°, *concentrations being expressed in grams of fatty anhydride and grams of salt per* 100 *grams of total system. The areas correspond to those in Fig.* 1.

to form " middle soap " or " neat soap " can exist and even half the isotropic field has been destroyed. At a temperature only about 10° lower, the solubility of sodium palmitate is reduced to an extremely narrow field of lye—along the bottom of the diagram, with curd fibres at the top, all in between being wet curds with enmeshed lye. At room temperature, sodium palmitate is practically insoluble and the only systems met with are wet and dry curds. The diagram shows two (approximate) solubility curves for 72° and 76°, respectively, and there are also dotted in the boundary

lines of the liquid phases at 80°, at which temperature the solubility of sodium palmitate is so much greater that neat soap is the only form of liquid concentrated enough to be capable of crystallising.

Figs. 4 and 5 present the data for the accurate mapping of the limits of the field of isotropic solutions at temperatures ranging from 60° to 150°. The solutions at 60° are of course under-cooled with respect to separation of curd fibres.

FIG. 3.



Maximum concentrations of solutions which can exist at 76° (*and at* 72°) *when not supersaturated with curd fibres. The fields enclosed by the dotted lines within the shaded areas are soap solutions which have been destroyed by the curd fibres crystallising out at* 76°.

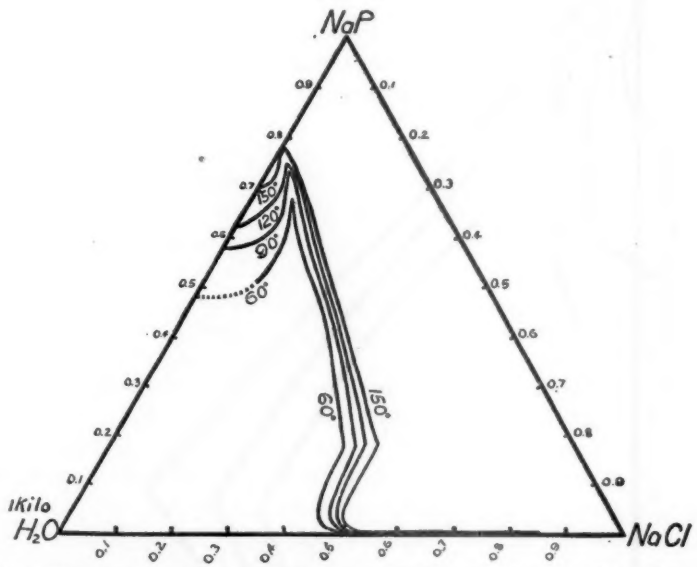
The diagram at 150° is particularly interesting because it shows the concentrations of solutions of pure soap in the absence of salt at which isotropic solutions, "middle soap" and "neat soap" exist. Up to $2{\cdot}3N_w$ at 150°, solutions of sodium palmitate are isotropic. Solutions slightly more concentrated cannot be made owing to the separations of "middle soap." "Middle soap" exists between the concentrations $2{\cdot}5N_w$ and $3{\cdot}0N_w$ and this is nearly the maximum temperature at which "middle soap" can exist at all. It is remarkable that in still higher concentrations isotropic solutions are again formed and the diagrams show clearly

how these concentrated isotropic solutions continuously pass through the solutions containing salt to the dilute isotropic solutions. At still higher concentrations of aqueous sodium palmitate, the further anisotropic phase, " neat soap," is formed.

*Outline of Previous Work.**

Chevreul's view that a bar of soap consists of definite hydrates has been maintained even by Lewkowitsch, who speaks of " water of constitution." Merklen attacked this, assuming that such soap

FIG. 4.



Solubility curves of salt and sodium palmitate at 60°, 90°, 120° *and* 150° *showing the extreme limits of the field of homogeneous isotropic solutions capable of existing at these temperatures.*

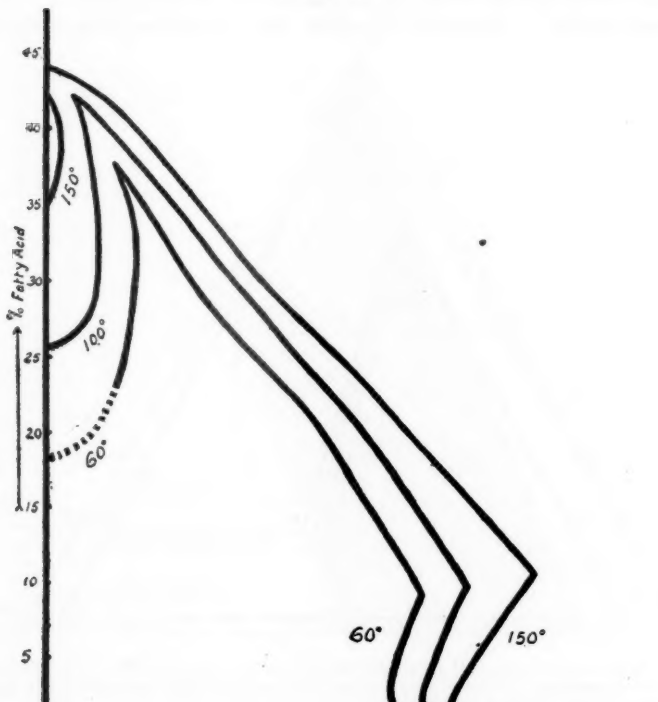
is a " sorption compound." Since such a bar, whether of household soap or toilet base, is obtained merely by the cooling of neat soap removed from the soap pan, we see, however, that, although its total composition is necessarily that of the original sample of " neat soap," its constitution and structure have nothing to do with those of " neat soap." Actually it is a heterogeneous mixture, consisting of innumerable hydrated curd fibres enmeshing one or more solutions containing the more soluble soaps. The bar of soap is thus a heterogeneous mixture necessarily of the same total

* See Fourth Colloid Report of the British Association for the Advancement of Science, 1922, 249.

composition as the "neat soap" which was taken from the soap pan.

Merklen's monograph in 1907 constituted a great advance in the scientific treatment of this subject in that it was the first attempt to apply the phase rule to the soap-boiling processes. Merklen worked with commercial soaps and oils and recognised two of

FIG. 5.



Limits of existence in technical units of homogeneous isotropic solutions containing salt and soap at 60°, 100°, *and* 150° *showing the two regions in which solutions of pure soap form isotropic solutions at* 150°.

the systems here described, namely, "neat soap" with "nigre" and "lye," respectively. It appears, however, that his soap-boiling technique was faulty in that he did not secure proper separation.

Richert (*Diss.*, Karlsruhe, 1911), working with dilute solutions of pure soaps, discovered the two-layer system "nigre-lye." He was the first to show that various salts have a similar effect so that

by the use of numerical factors it is possible to predict the amounts of each which will replace the others.

Further, it is evident from scattered information, published and unpublished, there is little or no fractionation when mixtures of soaps separate into liquid layers. Hence it is evident that as far as formation of liquid layers is concerned the most complicated mixture of commercial oils and fats containing a number of electrolytes such as hydroxide, carbonate, chloride, sulphate, etc., exhibits a behaviour similar to that of a three-component system such as is described in the present paper. It is only when sufficient salt has been added to cause a separation of some of the least soluble soaps as curd fibres that fractionation of the soaps sets in and the behaviour is that of a more complicated system. Fortunately, as has been seen, this occurs only to a minor extent in the soap pan, since graining out is never carried to completion.

Bätz (*Diss.*, Karlsruhe, 1918) and M. Thörl (*Diss.*, Karlsruhe, 1918) worked with commercial oils, studying neat soap together with lye or nigre or both. They considered that the three layers simultaneously present were not of fixed composition, but we can attribute this to a form of experiment in which equilibrium was not perfectly attained. Their results, like those for other published data on analysis of commercial products, agree essentially with the triangular diagram explained in this paper; but, not knowing of the existence of " middle soap," they regarded " neat soap " and " nigre " as continuous with each other instead of being wholly separate phases. The present paper and the previous one with Burnett show that the total number of possible two-layer systems is seven. The present paper has been written with a knowledge of further comprehensive experiments carried out in this laboratory by A. V. Pitter and W. J. Elford, and others.

One single example may be given to illustrate the usefulness of the phase rule diagrams developed in our present paper. Bergell (*Seifens. Ztg.*, 1924, **51**, 591) has published technical experiments on a commercial scale which seemed to show that in passing from a very close fit to a very open fit the amount of salt in the neat soap passed through a minimum. For a very close fit or for a very open fit the quantity of salt in the upper layer was 1%, whereas for a fit intermediate between that customary for soap base and bar soap only 0·3% of salt was present. It is obvious from purely geometrical considerations that it is impossible to place such a curve as that found by Bergell upon the diagrams given in the present paper or upon any of the numerous diagrams of similar types for commercial soaps without cutting across the lines or, in other words, without entering the heterogeneous region of the two-layer system, neat

soap-nigre. It follows with certainty that the result obtained by Bergell was due to faulty or incomplete separation of nigre and neat soap in the closer fits.

Summary.

1. For the first time a complete survey has been made of the stable systems of water, soap and salt.

2. The following phases can exist in any soap system, whether prepared from a commercial oil or from pure soap; true lamellar crystals; crystalline curd fibres; anisotropic liquid "neat soap"; anisotropic liquid "middle soap" (existence previously unsuspected); isotropic liquid. All the soap-boiling operations depend on equilibria between these phases.

3. The limits of the field of existence of isotropic liquid solutions of sodium palmitate with and without salt have been accurately determined for temperatures up to 150°. This single phase includes wholly crystalloidal and wholly colloidal solutions and ranges at sufficiently high temperatures from pure water up to pure anhydrous liquid sodium palmitate, the two being miscible in all proportions above 316°.

4. As a first and close approximation the contents of a soap pan, although prepared from commercial oils and fats each containing many constituents, and although containing many electrolytes, behaves like a simple three-component system apart from crystallisation.

In conclusion, our thanks are due to the Colston Research Society of the University of Bristol and to the Chemical Society for grants for materials.

THE UNIVERSITY, BRISTOL. [*Received, February 18th*, 1925.]

CXXI.—*The Nature of the Alternating Effect in Carbon Chains. Part II. The Directing Influence of the α-Methoxyvinyl Group in Aromatic Substitution.*

By CHRISTOPHER KELK INGOLD and EDITH HILDA INGOLD.

As explained in Part I (this vol., p. 513), these investigations have been undertaken in order to obtain insight into the nature of the alternating effect, the existence of which is implied both in the hypothesis of alternating affinity-demand and in the hypothesis of induced polarities.

For the present, attention is being confined to directive influence in aromatic substitution, and in Part I it was shown that the

nitroso-group falls within the *op*-directing series. The nitroso-group is one of the very few groups as to the directive effect of which the theories of alternating affinity and induced polarity appear to differ in their predictions; and the observed facts agree with the idea of alternating affinity rather than with that of induced polarity, unless, indeed, in the latter case, such flexibility of procedure be admitted as would completely destroy the prophetic power of this theory in all potential test-cases.

Since the above facts were communicated, three arguments have been advanced in the cause of the polarity theory:

(i) That since in the nitroso-group there are two competing negative key-atoms, the case is too complicated for satisfactory prediction (Lapworth, *Chem. and Ind.*, 1924, **43**, 1294).

(ii) That oxygen, although "usually" more negative (or negatively active) than nitrogen, suffers handicap in the nitroso-group owing to the greater distance of the oxygen atom from the benzene ring (*idem*, *ibid.*).

(iii) That a different mechanism may (should ?) be assumed when the atom directly attached to the benzene ring contains a "lone-pair" of electrons (Robinson, *ibid.*, p. 1297).

There are logical answers to all these objections,* but it is perhaps of greater importance that they are amenable to experimental treatment; and experiments are now described which were devised as a test of their validity.

A substituent group was selected to fulfil the following conditions:

(*a*) That opposite forecasts as to its directive effect shall flow from the simple application of the principles of alternating affinity and induced polarity (*vide* Part I, *loc. cit.*).

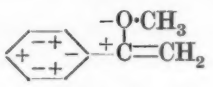
(*b*) [*Condition to obviate objections* (i) *and* (ii).] That either the group shall contain only one negative key-atom, or, if there be several, these shall be harmoniously situated.

(*c*) [*Condition to obviate objection* (iii).] That the atom by which the group is attached to the benzene ring shall not contain a "lone-pair" of electrons.

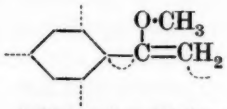
It may be stated at once that even when these conditions are fulfilled orienting effects are observed which still agree with the idea of alternating affinity, and still run counter to that of induced polarity.

* Arguments (i) and (ii) apply equally to the nitro- and ammonium-salt groups ($-NO_2$ and $-NH_3X$), which happen to behave satisfactorily from the polarity point of view. Thus, in advancing these two arguments, a great part of the case for the polar conception of orienting action is given away. The logical reply to (iii) has been made by Flürscheim (*Chem. and Ind.*, 1925, **44**, 33, 34).

Condition (*c*) was secured by making the connecting atom a carbon atom, condition (*b*) by attaching to it only one oxygen atom (and, of course, no nitrogen atom), and condition (*a*) by introducing a double bond, the residual affinity from which determines the effect to be expected from the theory of alternating affinity (compare Flürscheim, *J. pr. Chem.*, 1902, **66**, 321). The combined result of these structural requirements is represented in the α-methoxyvinyl group, the predicted orienting effects of which are expressed in the following formulæ:



(Alternate polarities: *m*-directive action.)



(Alternating affinity: *op*-directive action.)

The directing influence of the α-methoxyvinyl group in nitration is practically exclusively ortho-para; that is to say, it is in agreement with the hypothesis of alternating quantity of affinity.

It should be added that certain results are capable of interpretation on the basis that a nitro-group first enters the ω-position, giving (I), which then, on further nitration, yields (II) and (III):

(I.) $C_6H_5\cdot C(OMe){:}CH\cdot NO_2 \longrightarrow \begin{cases} (o)NO_2\cdot C_6H_4\cdot C(OMe){:}CH\cdot NO_2 \text{ (II.)} \\ (p)NO_2\cdot C_6H_4\cdot C(OMe){:}CH\cdot NO_2 \text{ (III.)} \end{cases}$

If this were so, the real directing group to which the products (II) and (III) owe their formation would not be $-C(OMe){:}CH_2$, as intended, but $-C(OMe){:}CH\cdot NO_2$. This, however, would not explain the lack of agreement with the application of alternate polarities, because on attaching to the atoms of the nitro-group those plus and minus signs which best explain its general behaviour from the polarity standpoint, it is at once seen that this group, far from competing with, would actually reinforce, the key-negative influence of the ethereal oxygen.

Conclusion.—The inference recorded in Part I appears to be confirmed by these experiments.

Experimental.

α-Methoxystyrene was prepared from ethyl phenylpropiolate by a series of reactions analogous to those investigated by Moureu (*Compt. rend.*, 1904, **137**, 260; *Bull. Soc. chim.*, 1904, **31**, 498, 525; see also Claisen, *Ber.*, 1898, **31**, 1020).

Ethyl phenylpropiolate (50 g.) was heated for 2 hours on the water-bath with 140 c.c. of methyl-alcoholic sodium methoxide prepared from 6·9 g. of sodium. The oil, b. p. 140—147°/10—

11 mm., extracted with ether after pouring into ice-water consisted principally of a mixture of methyl and ethyl ββ-dimethoxy-β-phenylpropionates, containing, however, traces of the β-methoxycinnamates. Without purification, the oil was converted into a mixture of methyl and ethyl methoxycinnamates by heating in an oil-bath at 200° for 1 hour, when methyl alcohol was evolved. The mixed esters, b. p. 144—149°/8 mm., were then hydrolysed by hot aqueous-alcoholic potassium hydroxide, exactly as described by Moureu in the case of methyl methoxycinnamate, and the free acid, after due purification, was converted by heat and subsequent distillation into α-methoxystyrene.

Nitration of α-Methoxystyrene.—The methoxystyrene (5 g.) was allowed to flow through a capillary tube during about 30 hours into 22·5 g. of pure nitric acid kept at — 20° and well shaken. The product was isolated by pouring on to ice and extracting with ether. Washing with aqueous sodium carbonate removed a small quantity of a yellow, crystalline, acidic substance, which has not yet been investigated, and the residual ether solution yielded a yellow oil, which could be distilled without decomposition only at about 1 mm. Three principal fractions were obtained, (*a*) an almost colourless, mobile oil, b. p. below 60°, (*b*) a fairly mobile, yellow oil, b. p. 88—95°, (*c*) a rather viscous, yellow oil, b. p. 128—132° (chief fraction).

Fraction (*a*) contained qualitative traces of nitrogen, but consisted chiefly of acetophenone, the normal hydrolysis product of α-methoxystyrene.

Fraction (*b*) was a mixture consisting apparently of the mononitration products of α-methoxystyrene and acetophenone. The quantity was too small to permit of a detailed investigation, but on oxidation with potassium permanganate benzoic acid and the three nitrobenzoic acids were obtained.

Fraction (*c*) contained the dinitration products. On redistillation, it gave no indication of separating into fractions, almost the whole passing over at 128—130°/1 mm. The figures obtained on analysis (Found: C = 48·5; H = 3·6. $C_9H_8O_5N_2$ requires C = 48·2; H = 3·6%) corresponded with those required for a dinitromethoxystyrene, but all attempts to crystallise it proved fruitless. It was observed, however, that all the α-alkyloxystyrenes described in the literature are liquids, even those of fairly high molecular weight like α-phenoxy- and the three α-tolyloxy-styrenes, and it was therefore decided to determine the constitution of the oil by oxidation. The results of these experiments show that it consists to the extent of about 65% of ω*p*-dinitro-α-methoxystyrene, the remainder being the isomeric ω*o*-compound.

Oxidation of ωo-*Dinitro-α-methoxystyrene and* ωp-*Dinitro-α-methoxystyrene* (II *and* III).—The mixture of these isomerides (2·5 g.) was thoroughly emulsified with a little water and then vigorously shaken in the cold with successive small quantities of a solution of 20 g. each of potassium permanganate and sodium hydrogen carbonate in 1 litre of water, the additions being timed to keep pace with decoloration. When 50 c.c. had been added, the mixture was transferred to the steam-bath, and the addition of permanganate solution continued. No great diminution in the velocity of the reaction was noticed when 200 c.c., the theoretical amount for the formation of $NO_2 \cdot C_6H_4 \cdot CO_2Me + CO_2 + HNO_3$, had been added, and the process was therefore continued until 370 c.c. had been used, and the product was relatively stable to permanganate. The small excess of the reagent was removed with hydrogen peroxide, and the solution filtered. The precipitate was thrice suspended in water and treated with steam, and the combined filtrates were extracted with ether, evaporated to small bulk, and acidified. The small oily residue obtained on evaporating the ethereal extract was boiled for 16 hours with 20% hydrochloric acid, and the resulting solution made alkaline, extracted with ether, and reacidified. After combining the two acid solutions, the organic acids were isolated by extraction with ether.

The residue from the ether was distilled in steam for a short time, and the absence of benzoic acid proved by examining the first portions of the distillate. It was then crystallised from much boiling water, from which, on cooling, nearly pure *p*-nitrobenzoic acid separated, m. p. 230—234°. This was finally purified by crystallisation from glacial acetic acid, and identified by its m. p. (237—238°), by analysis (Found: C = 50·6; H = 3·2. Calc., C = 50·3; H = 3·0%), by direct comparison and mixed m. p. with a genuine specimen, and by conversion into its methyl ester (m. p. 96°), which was similarly compared.

The mother-liquors contained a much more soluble acid, m. p. about 140—143°, which, from mixed m. p. determinations with *o*-nitrobenzoic acid (m. p. 146—147°) and *m*-nitrobenzoic acid (m. p. 140—141°), appeared to consist mainly of *o*-nitrobenzoic acid. In order to detect any *m*-nitrobenzoic acid, if present, the specimen was treated successively with phosphorus pentachloride and methyl alcohol, the methyl esters being isolated by extraction with pure ether after addition of water. Since methyl *m*-nitrobenzoate is crystalline and sparingly soluble in cold methyl alcohol, whilst methyl *o*-nitrobenzoate is a liquid completely miscible with that solvent, any *m*-ester present should have separated when methyl alcohol was added to the mixed esters and seeded with a

crystal of the *m*-ester; for experiments with artificial mixtures of the two isomerides indicated this method to be an efficient one for the detection and separation of small quantities of the *m*-compound. In the case under description, however, no separation of *m*-ester occurred, although a very small quantity of methyl *p*-nitrobenzoate crystallised. The liquid ester was therefore rehydrolysed with hydrochloric acid, and the *o*-nitrobenzoic acid so obtained crystallised from dilute acetic acid and identified by its m. p. (146—147°), analysis (Found: C = 50·5; H = 3·2. Calc., C = 50·3; H = 3·0%), and comparison with an authentic specimen.

Treatment of Fraction (*b*).—The oxidation of this fraction by permanganate was carried out as in the preceding experiment, and the various acids so produced were separated in a similar way. Benzoic acid was isolated by distillation in steam, *p*-nitrobenzoic acid by crystallisation from water, whilst the more soluble but less volatile *o*- and *m*-acids were separated through their methyl esters as described above (for methyl *m*-nitrobenzoate, m. p. 79°, found: C = 53·1; H = 4·1. Calc., C = 53·0; H = 3·9%).

Treatment of Fraction (*a*).—On redistillation, this yielded a colourless oil, b. p. 88—92°/12 mm., which was identified as acetophenone by means of its semicarbazone. The latter was prepared using semicarbazide acetate and crystallised from ethyl alcohol, from which needles separated, m. p. 200°, which did not depress the m. p. of a genuine specimen of acetophenonesemicarbazone.

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CXXII.—*Bromo-derivatives of* m-*Hydroxybenzaldehyde.*

By HERBERT HENRY HODGSON and HERBERT GREENSMITH BEARD.

ALTHOUGH the 6-bromo-derivative (Pschorr, *Annalen*, **1912, 391**, 23) and the 2 : 4 : 6-tribromo-derivative (Krause, *Ber.*, **1899, 32**, 122) have been described, little attention has hitherto been directed to the bromination of *m*-hydroxybenzaldehyde.

Tribromination of the aldehyde in aqueous solution at 50° is sufficiently quantitative to be suitable for its estimation, and regulated bromination to the 6-mono-, 4 : 6-di-, and 2 : 4 : 6-tribromo-derivatives can be carried out in chloroform or carbon tetrachloride; Rosenmund, Kuhnhenn, and Lesch's method of moderated bromination in presence of a quinoline salt (*Ber.*, **1923, 56, 2042**) does not give better results.

2-, 4-, and 6-Bromo-3-hydroxybenzaldehydes were prepared synthetically from *m*-hydroxybenzaldehyde *via* the corresponding nitro-compounds. In the nitration, good yields of 6- and 4-nitro-3-hydroxybenzaldehydes were obtained, but to isolate the 2-nitro-compound superheated steam was required and its use was attended with considerable destruction of material. The silver salts of these nitro-compounds have characteristic colours and differ in stability towards boiling water. Only poor yields of 6-bromo-3-hydroxybenzaldehyde were obtained from the 6-nitro-compound, and these are attributed to secondary changes occurring during the reduction stage—the amino-compound is readily oxidised and is converted by hydrochloric acid into a red amorphous substance corresponding with the formula $HO{\cdot}C_6H_3<\overset{CH}{\underset{N}{\|}}$ (it is noteworthy that Friedländer prepared 6-chloro-3-hydroxybenzaldehyde from the nitrocresol, not from 6-nitro-3-hydroxybenzaldehyde).

An attempt to introduce bromine into the *p*-nitrophenylhydrazone of 4-amino-3-hydroxybenzaldehyde by the Sandmeyer reaction led to the ready production of *p*-nitrophenylazoimide, and therefore to work (now in progress) on the decomposition of hydrazones.

The colours of the *p*-nitrophenylhydrazones of the various hydroxy-aldehydes are for the most part in agreement with Chattaway and Clemo's generalisation (J., 1923, **123**, 3041); their methyl ethers are yellower in shade and have the same colour in alkaline solution. In general the m. p.'s of the ethers are lower than those of the hydroxy-aldehydes.

Experimental.

Direct Bromination of m-*Hydroxybenzaldehyde.*—In aqueous solution it was impossible to regulate the bromination, and rapid addition of excess of bromine in the cold gave an incompletely tribrominated product (Found : Br, 62·6. Calc., Br, 66·8%). Careful addition at 50°, however, gave pure 2 : 4 : 6-tribromo-3-hydroxybenzaldehyde of m. p. 119° (Krause), although rapid addition still produced mixtures. Brominated at 50° by the standard bromide-bromate method with very cautious acidification, 0·2421 g. of *m*-hydroxybenzaldehyde absorbed 0·4684 g. of bromine (equiv. to 2·9 atoms).

Regulated bromination in chloroform. A solution of *m*-hydroxybenzaldehyde (10 g. in 100 c.c. of chloroform) was treated with the calculated quantity (for monobromination) of bromine in 30 c.c. of chloroform. The crude product (15 g.), after extraction with 50 c.c. of 6% sodium carbonate solution and crystallisation from dilute acetic acid, gave 6-bromo-3-hydroxybenzaldehyde,

m. p. 134° (compare Pschorr, *loc. cit.*). A blackish-green by-product containing bromine was insoluble in dilute acetic acid but dissolved in aqueous sodium hydroxide. On acidification of the sodium carbonate extract (above) a mixture of 6- and 4-bromo-3-hydroxybenzaldehydes was precipitated; these were converted into the *p*-nitrophenylhydrazones, which were separated by fractional crystallisation from chloroform, that of the 6-bromo-compound being the less soluble.

With the quantities of bromine and solvent given above, the 6- and the 4-bromo-compound were each converted into 4 : 6-dibromo-3-hydroxybenzaldehyde, m. p. 139°. The temperature was slowly raised to 50°, when hydrogen bromide was evolved. The mixture was heated under reflux for 1 hour, and the crude product, m. p. 138°, recrystallised from dilute acetic acid. There were no by-products (Found : Br, 57·4. Calc., Br, 57·2%).

2 : 4 : 6-Tribromo-3-hydroxybenzaldehyde, m. p. 119°, was obtained in like manner.

Regulated bromination in carbon tetrachloride. The crude monobromo-compound melted at 132—133° and no by-product was formed (Found : Br, 40·4. Calc., Br, 39·8%). Since, however, 5 g. of *m*-hydroxybenzaldehyde dissolve in 200 c.c. of carbon tetrachloride and in 75 c.c. of chloroform, the use of the latter solvent is preferable in bulk preparations.

The crude product obtained by the method of Rosenmund, Kuhnhenn, and Lesch (*loc. cit.*) melted at 128—130°.

Preparation of the Mononitro-3-hydroxybenzaldehydes.—Pschorr's method of nitration (*loc. cit.*; see also Friedländer, *Ber.*, 1914, **47**, 3040) was modified only in that a solution of twice the concentration was used. The yield of precipitated nitro-compounds was 117 g. from 100 g. of *m*-hydroxybenzaldehyde; 8 g. more were salted out from the mother-liquor. From the total product, 48 g., 32 g., and 5 g. of 6-, 4-, and 2-nitro-3-hydroxybenzaldehyde, respectively, were obtained.

The *silver* salts of 6-, 4-, and 2-nitro-3-hydroxybenzaldehyde form light brownish-yellow leaves (Found : Ag, 38·9), brick-red plates (Found : Ag, 39·1), and dark red needles (Found : Ag, 38·94. Calc., Ag, 39·4%), respectively. The first is soluble in hot water, but decomposes rapidly in a boiling solution. The second is almost insoluble in cold water and is stable in a hot solution. The third is soluble in cold water and is less stable than the first.

Preparation of the Bromo-3-hydroxybenzaldehydes.—The preceding nitro-compounds were reduced by the following method. A suspension of 5 g. in 50 c.c. of water was treated gradually with 20 g. of solid sodium hyposulphite, and the mixture was heated on the

water-bath for 15 minutes, cooled, carefully acidified with hydrobromic acid, and treated as in the Sandmeyer reaction; the product was extracted with ether.

From 6-nitro-3-hydroxybenzaldehyde, 6-bromo-3-hydroxybenzaldehyde was obtained in but poor yield. After crystallisation from dilute acetic acid, it melted at 133—134°, alone or mixed with the corresponding bromo-compound obtained from *m*-hydroxybenzaldehyde. Attempts to improve the yield by reducing with ferrous sulphate and ammonia, or by reduction of various derivatives of 6-nitro-3-hydroxybenzaldehyde (acyl derivatives, oxime, acylated oxime, etc.) were unsuccessful.

In the preparation of 4-*bromo*-3-*hydroxybenzaldehyde* from the nitro-compound it was found advantageous, after the reduction, to diazotise the product in hydrochloric acid, add sodium acetate, and then follow the usual Sandmeyer procedure. The 4-bromo-compound, m. p. 131·5°, is only slowly volatile in steam and is partly decomposed thereby (Found : Br, 39·2. $C_7H_5O_2Br$ requires Br, 39·8%).

2-*Bromo*-3-*hydroxybenzaldehyde* melts at 141—142° (Found : Br, 39·5%).

p-*Nitrophenylazoimide*. — 4-Amino-3-hydroxybenzaldehyde-*p*-nitrophenylhydrazone was diazotised in hydrochloric acid, and the product decomposed on the water-bath with cuprous chloride. Distillation with steam removed *p*-nitrophenylazoimide, which melted at 69·5° after crystallisation from alcohol (Found : N, 34·7. Calc., N, 34·1%).

Preparation of 6-, 4-, *and* 2-*Bromo*-3-*methoxybenzaldehydes*.—The corresponding hydroxy-aldehyde (1 mol.), dissolved in boiling 10% sodium hydroxide solution (2 mols.), was treated with methyl sulphate (1·3 mols.). After 1 hour, the mixture was distilled with steam, and the methoxy-compound, which separated from the distillate on cooling, recrystallised from dilute alcohol. 6-Bromo-3-methoxybenzaldehyde melts at 76° (Pschorr gives m. p. 76°), the 4- and the 2-bromo-compound at 74° and 45—46°, respectively.

These compounds were also prepared from the corresponding nitromethoxybenzaldehydes. The nitro-compound (10 g.), dissolved in boiling alcohol (50 c.c.), was treated with sodium disulphide (14 g. of cryst. sodium sulphide, 3·5 g. of sulphur, 15 c.c. of water). After boiling for 3 hours, the solution was diluted, and extracted with ether. The residue after evaporation of the ether was dissolved in 10 c.c. of alcohol, and 10 g. of sulphuric acid (50%) were added,*

* If the acid is added to the free amine obtained from the ether extract, a hard, insoluble, red substance is produced (compare Khotinsky, *Ber.*, 1909, **42**, 3097).

when the finely-divided sulphate of the amine was obtained. (The sulphate of 4-amino-3-methoxybenzaldehyde has a brilliant red colour which fades on keeping; the sulphate of 4-amino-3-hydroxybenzaldehyde behaves similarly.) The sulphate was diazotised, and the product treated with cuprous bromide.

6-Bromo-3-methoxybenzaldehyde was thus obtained from the 6-nitro-compound in good yield (in sharp contrast to the trace of 6-bromo-3-hydroxybenzaldehyde obtained from 6-nitro-3-hydroxybenzaldehyde). The yield of the 4-bromo-compound (Found: Br, 37·0%) was 4 g. from 10 g. of 4-nitro-3-methoxybenzaldehyde. The 2-bromo-compound formed fine white needles (Found: Br, 37·2%). All three products were contaminated with oily impurities which were probably substances of the anthranil type.

4 : 6-*Dibromo*-3-*methoxybenzaldehyde*, obtained by methylation of the hydroxy-compound in aqueous sodium hydroxide, melted at 110° after crystallisation from dilute alcohol (Found: Br, 53·8. $C_8H_6O_2Br_2$ requires Br, 54·4%).

Oximes of the Nitro- and Bromo-hydroxybenzaldehydes and of the Bromomethoxybenzaldehydes.

General Method of Preparation.—An alcoholic solution of the aldehyde (1 mol.) was treated with aqueous hydroxylamine hydrochloride (1 mol.) and sodium acetate, the mixture boiled for 1 hour, and the oxime allowed to crystallise from the cooling and slowly evaporating solution.

6-*Nitro*-3-*hydroxybenzaldoxime*: Pale yellow needles by addition of light petroleum to an ethereal solution; m. p. 178—179° (the m. p. of the oxime crystallised from water is never higher than 172°) (Found: N, 15·35. $C_7H_6O_4N_2$ requires N, 15·4%). Yellow sodium salt.

4-*Nitro*-3-*hydroxybenzaldoxime*: Deep yellow needles, m. p. 164° (Found: N, 15·6%). Brilliant red sodium salt, sparingly soluble in water.

2-*Nitro*-3-*hydroxybenzaldoxime*: Needles paler than the preceding; m. p. 172·5° (Found: N, 15·6%). Much more difficult to prepare than either of the preceding oximes. Sodium salt not so vividly red as that of the 4-nitro-compound.

6-*Bromo*-3-*hydroxybenzaldoxime*: White needles from water; m. p. 157° (Found: Br, 36·5. $C_7H_6O_2NBr$ requires Br, 37·0%). Pale yellow sodium salt.

4-*Bromo*-3-*hydroxybenzaldoxime*: White, microcrystalline powder from water; m. p. 173—174° (Found: Br, 36·6%).

2-*Bromo*-3-*hydroxybenzaldoxime*: Fine, white needles from water; m. p. 148° (Found: Br, 36·7%).

4 : 6-*Dibromo*-3-*hydroxybenzaldoxime :* m. p. 243° (Found : Br, 54·0. $C_7H_5O_2NBr_2$ requires Br, 54·2%).

6-*Bromo*-3-*methoxybenzaldoxime :* Silky, white needles from dilute alcohol; m. p. 117° (Found : Br, 34·8. $C_8H_8O_2NBr$ requires Br, 34·75%).

4-*Bromo*-3-*methoxybenzaldoxime :* White needles, m. p. 94·5° (Found : Br, 34·9%).

2-*Bromo*-3-*methoxybenzaldoxime :* White needles, m. p. 148° (Found : Br, 34·2%).

Carboxylic Acids from the Bromomethoxybenzaldehydes.

General Preparation.—The aldehyde (1 mol.) was heated for 2 hours on the water-bath with a solution of potassium permanganate (0·66 mol.) and sodium carbonate. The solution was treated with sodium bisulphite, acidified with hydrochloric acid, and the product recrystallised from water.

6-Bromo-3-methoxybenzoic acid : White needles, m. p. 162° (Pschorr gives m. p. 162°).

4-*Bromo*-3-*methoxybenzoic acid :* White needles, m. p. 219—220° (Found : Br, 34·5. $C_8H_7O_3Br$ requires Br, 34·6%).

2-Bromo-3-methoxybenzoic acid : White needles, m. p. 157—158° (Pschorr gives m. p. 153—155°. His product probably contained the 4-bromo-acid as impurity) (Found : Br, 34·4%).

4 : 6-Dibromo-3-methoxybenzoic acid : Stout, white needles from dilute alcohol; m. p. 202—203° (Bauer and Vogel, *J. pr. Chem.*, 1913, **88**, 329, give m. p. 201—202°).

The p-*Nitrophenylhydrazones.*

General Preparation.—The aldehyde, dissolved in rather dilute acetic acid, was treated gradually with an aqueous solution of *p*-nitrophenylhydrazine until precipitation ceased. The hydrazone was formed in quantitative yield. The method is generally applicable to the estimation of aldehydes. A hydrazone precipitated from aqueous solution is paler in colour than the same hydrazone crystallised from alcohol, chloroform, or acetone. The hydroxy-hydrazones all exhibit a colour change when heated, becoming paler at 150—160°; the colour returns just prior to fusion, when decomposition occurs. The methoxy-hydrazones behave normally and are stable when heated. (The colour produced by addition of alcoholic potassium hydroxide to an alcoholic solution of the hydrazone is given immediately after the m. p.)

6-*Nitro*-3-*hydroxybenzaldehyde*-p-*nitrophenylhydrazone :* Deep orange-red needles; decomp. 250°, m. p. above 300°. Reddish-violet (Found : N, 18·9. $C_{13}H_{10}O_5N_4$ requires N, 18·5%).

4-*Nitro*-3-*hydroxybenzaldehyde*-p-*nitrophenylhydrazone :* Redder orange than the preceding; m. p. 265—266°. Bluish-violet.

2-*Nitro*-3-*hydroxybenzaldehyde*-p-*nitrophenylhydrazone :* Brick-red needles, m. p. 240—250° (decomp.). Reddish-violet (Found : N, 19·0%).

4-*Nitro*-3-*methoxybenzaldehyde*-p-*nitrophenylhydrazone :* Brick-red needles, m. p. 236—238°. Violet-blue, very different from the other colours and in accord with Chattaway's observation (*loc. cit.*) with regard to two nitro-groups in para positions (Found : N, 17·8. $C_{14}H_{12}O_5N_4$ requires N, 17·7%).

There was no change in colour on heating any of the above alcoholic solutions.

6-*Bromo*-3-*hydroxybenzaldehyde*-p-*nitrophenylhydrazone :* Reddish-orange needles, m. p. 240—243°. Deep claret (Found : Br, 23·9. $C_{13}H_{10}O_3N_3Br$ requires Br, 23·8%).

The 4-*bromo*-isomeride : Brick-red needles, m. p. 210—212°. Decomp. above 220°. Deep claret (Found : Br, 23·7%).

The 2-*bromo*-isomeride : Red needles, m. p. 241°. Deep claret (Found : Br, 23·2%).

The claret shade is deepest for the 4-bromo- and lightest for the 6-bromo-compound.

6-*Bromo*-3-*methoxybenzaldehyde*-p-*nitrophenylhydrazone :* Orange needles, m. p. 225°. No decomp. Deep claret (Found : Br, 22·3. $C_{14}H_{12}O_3N_3Br$ requires Br, 22·8%).

The 4-*bromo*-isomeride : Orange needles, m. p. 246°. No decomp. Deep claret (Found : Br, 22·3%).

The 2-*bromo*-isomeride : Yellow needles, m. p. 206—208°. No decomp. Deep reddish-violet bordering on purple (Found : Br, 22·6%).

Again the 4-bromo-compound gives the deepest, and the 6-bromo-compound the lightest claret shade. These colours are as deep as those of the corresponding hydroxy-compounds. The hydroxyl groups of the latter therefore have no effect on the colour.

4 : 6-*Dibromo*-3-*hydroxybenzaldehyde*-p-*nitrophenylhydrazone :* Dull brick-red needles, m. p. 259—260° (decomp.). Colour fades at 200°. Deep reddish-violet (Found : Br, 38·0. $C_{13}H_9O_3N_3Br_2$ requires Br, 38·5%).

2 : 4 : 6-*Tribromo*-3-*hydroxybenzaldehyde*-p-*nitrophenylhydrazone :* Deep brick-red needles, m. p. 229—230° (decomp.). Deep reddish-violet.

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CXXIII.—*The Hydrolysis of Iodine as Measured by the Iodine Electrode.*

By Humphrey Desmond Murray.

To account for the hydrolysis of iodine in aqueous solution, it is convenient to postulate some degree of dissociation. The simplest case is the production of two oppositely charged ions from the diatomic iodine molecule. Hydrolysis follows from the reaction:

$$I^{\cdot} + H_2O = H^{\cdot} + HIO.$$

In solution there is, then, between the iodine and hypoiodous acid molecules and the ions $H^{\cdot}$, $I^{\cdot}$, I', and I_3', an equilibrium which is derivable from the mass-action laws: $[I^{\cdot}][I']/[I_2] = K_1$; $[I'][I_2]/[I_3'] = K_2$; $[I^{\cdot}][OH']/[HIO] = K_3$. Hence under conditions where any hydrogen iodide formed is largely dissociated,

$$K_1 = \frac{[I']^2}{[I_2]} \cdot \frac{1 + 1/K_2 \cdot [I_2]}{1 + K_w/K_3 \cdot 1/[H^{\cdot}]} \quad . \quad . \quad . \quad (1)$$

The object of this investigation was to determine, so far as possible, the value of K_1 by means of an iodine-iodide electrode. It was necessary that the solutions to be examined should be acid, in order to repress the formation of the iodate ion; and with the object of eliminating liquid junction potential differences, a mercurous sulphate electrode was adopted as a reference electrode. This made desirable a determination of the *E.M.F.* of this electrode against the hypothetical normal hydrogen electrode, or failing this, against the iodine electrode, for which accurate values have been recorded. The method adopted was to determine the normal electrolytic potential for the iodine electrode in N/10-potassium chloride against the N/10-calomel electrode, and then, employing concentrations of iodine and iodide of a similar order, measure the potential difference between the iodine electrode and the mercurous sulphate electrode.

The value of K_2 has been determined with considerable accuracy at different temperatures, but it was thought advisable to redetermine it for solutions containing potassium chloride and sulphuric acid. To this end, solutions of iodine in carbon tetrachloride were shaken with solutions of potassium iodide in N/10-potassium chloride and in N/10-sulphuric acid until the distribution of iodine between the two layers was constant. Preliminary determinations gave the values 84·1 and 81·9 for the distribution coefficients of iodine at 25° between carbon tetrachloride and N/10-potassium chloride and N/10-sulphuric acid, respectively, over a range of 0·0006—0·00004 mol./litre in the aqueous layer. Both methods

gave the same value for K_2 at 25° within the limits of experimental error: 0·001390 ± 0·000002. This is higher by about 0·000010 than the accepted value for pure aqueous solutions.

To determine the normal potential of the iodine electrode, successive weighed quantities of pure dry potassium iodide were dissolved in N/10-potassium chloride, and the resulting solution was shaken with iodine several times sublimed. The amount of iodine taken up was controlled to a certain extent by the length of time for which the solution was shaken. The iodine solutions were filtered through glass wool into the electrode vessels, and a portion was removed and titrated against thiosulphate. The electrodes were of platinum foil very slightly coated with platinum black. Measurements were made after the *E.M.F.* had been constant for about an hour. The results are given in Table I: C is the concentration of the potassium iodide added, in mols./litre; A, the total concentration of iodine found by titration, *i.e.*, $[I_2] + [I_3']$, in mols./litre; a, the activity coefficient of the iodide ion interpolated from Lewis's results ("Thermodynamics," Lewis and Randall, 1923). The concentrations of free iodine and iodide ion are calculated from the tri-iodide equilibrium.

TABLE I.

Pt. $xI_2|yKI + N/10\text{-}KCl|N/10\text{-}KCl|Hg_2Cl_2$. Hg. Temp. 25°.

$A \times 10^4$.	$C \times 10^3$.	$[I_2] = x$.	$[I'] = y$.	a.	E.	E^0.
5·707	6·764	0·0001032	0·006296	0·790	(*a*) 0·3039	0·6207
					(*b*) 0·3036	0·6204
4·304	6·764	0·0000767	0·006410	,,	(*a*) 0·2990	0·6201
					(*b*) 0·2996	0·6207
4·373	2·073	0·0001891	0·001825	0·793	(*a*) 0·3433	0·6206
					(*b*) 0·3430	0·6203
2·232	2·073	0·0000931	0·001943	,,	(*a*) 0·3325	0·6205
					(*b*) 0·3321	0·6201
					Mean	0·6204

$$E^0 = E' - \frac{0{\cdot}05911}{2} \log \frac{[I_2]}{a^2[I']^2} \quad . \quad . \quad . \quad (2)$$

E is the actual *E.M.F.* found, referred to the N/10-calomel electrode. E' is the potential of the iodine electrode referred to the normal hydrogen electrode, *i.e.*, E increased by 0·3351 volt, the value adopted by Lewis as the difference between the two. E^0 is the normal potential calculated from these results. Its mean value is 0·6204 volt. Lewis (*op. cit.*) quotes three determinations of this value, one recalculated from data given by Maitland (*Z. Elektrochem.*, 1906, **12**, 263) and two by Lewis and Faragher (unpublished work) and Gerke (*J. Amer. Chem. Soc.*, 1922, **44**, 1682). If these are made applicable to the free iodine electrode by adding 0·0849 volt, they become 0·6212, 0·6210, and 0·6202, respectively.

The mercurous sulphate required for the electrode was prepared electrolytically. The $N/10$-sulphuric acid (10 litres) was standardised with sodium carbonate, and the same solution was used throughout. As a check on the preparation, the mean value of the *E.M.F.* of the mercurous sulphate electrode measured against the hydrogen electrode in $N/10$-sulphuric acid was determined and found to be $E = 0{\cdot}7550$ volt. The value obtained by Lewis and Lacey (*J. Amer. Chem. Soc.*, 1914, **36**, 804) is $E = 0{\cdot}7546$ volt.

The iodine solutions were prepared as before, but the potassium iodide was dissolved in $N/10$-sulphuric acid. The results are given in Table II.

TABLE II.

Pt. $x\mathrm{I_2}|y\mathrm{KI} + N/10\text{-}\mathrm{H_2SO_4}|N/10\text{-}\mathrm{H_2SO_4}|\mathrm{Hg_2SO_4}$. Hg. Temp. 25°.

$A \times 10^4$.	$C \times 10^3$.	$[\mathrm{I_2}] = x$.	$[\mathrm{I'}] = y$.	α.	E.	E''.
38·52	29·13	0·0001990	0·02333	0·772	(*a*) 0·0688	0·6829
					(*b*) 0·0686	0·6827
4·993	3·163	0·0001645	0·002828	,,	(*a*) 0·0171	0·6829
					(*b*) 0·0165	0·6823
2·729	2·625	0·0000988	0·002451	,,	(*a*) 0·0198	0·6827
					(*b*) 0·0201	0·6830
1·239	2·401	0·0000476	0·002322	,,	(*a*) 0·0284	0·6833
					(*b*) 0·0286	0·6835
					Mean	0·6829

$$(E'' + E) = E^0 + \frac{0{\cdot}05911}{2} \log \frac{[\mathrm{I_2}]}{a^2[\mathrm{I'}]^2} \quad . \quad . \quad . \quad (3)$$

E is the actual *E.M.F.* measured. E'' is the potential of the mercurous sulphate electrode prepared with $N/10$-sulphuric acid, calculated from E and referred to the normal hydrogen electrode. The mean value is $E'' = 0{\cdot}6829$ volt. The value calculated from (isohydric) data recorded by Noyes and Stewart (*J. Amer. Chem. Soc.*, 1910, **32**, 1133), taking their mean value for the hydrogen-ion concentration in $0{\cdot}05M$-acid—0·0585, is 0·6820 volt.

The value of the potential of the iodine electrode in acid solution was now measured. Pure powdered iodine which had been sublimed several times was shaken with successive quantities of $N/10$-sulphuric acid, the solution filtered through glass wool into the electrode vessel, and a portion removed and titrated. To obtain reproducible results, it was found necessary to wash the electrodes very thoroughly if they had been previously used in potassium iodide solutions. By combining equations (1) and (2) there is obtained the expression,

$$\log K_1\left(1 + \frac{K_w}{K_3} \cdot \frac{1}{[\mathrm{H^\cdot}]}\right) = \frac{2}{0{\cdot}05911}(E^0 - E'' - E) + \log \frac{1}{a^2}(1 + 1/K_2 \,.\, [\mathrm{I_2}]),$$

which may be written

$$\log B = \frac{2}{0{\cdot}05911}(E_x - E) + \log (1 + 1/K_2 \,.\, [\mathrm{I_2}]) \quad . \quad . \quad (4)$$

where $B = K_1\left(1 + \frac{K_w}{K_3} \cdot \frac{1}{[H^\cdot]}\right)$ and $E_x = -0{\cdot}0559$. The values of a used in calculating the electrode potentials were obtained by interpolation from Lewis's values for the activity coefficient. They have been employed to facilitate comparison with his experimental work, but reference to equations (3) and (4) will show that, if measurements are made in such a solution that we may give to a the value assigned to it in obtaining E'', then the calculated concentration of the iodide ion, and hence of the quantity B, is independent of the value given to a. In calculating B on the basis of the mass action laws, we make the assumption, which appears to be approximately true, that the iodide ion is completely dissociated in $N/10$-sulphuric acid. The results are given in Table III.

TABLE III.

Pt. $x\mathrm{I}_2|y\mathrm{KI} + N/10\text{-}\mathrm{H}_2\mathrm{SO}_4|N/10\text{-}\mathrm{H}_2\mathrm{SO}_4|\mathrm{Hg}_2\mathrm{SO}_4$. Hg.

$A \times 10^5$.	E.	$B \times 10^8$.	$A \times 10^5$.	E.	$B \times 10^8$.
81·57	(*a*) 0·1880	0·89	9·06	(*a*) 0·1818	0·97
	(*b*) 0·1872	0·95		(*b*) 0·1818	0·97
27·19	(*a*) 0·1849	0·84	4·08	(*a*) 0·1793	1·14
	(*b*) 0·1843	0·89		(*b*) 0·1795	1·12
				Mean	0·97

A constant value for B is obtained, except in the most dilute solution. Now by combining the equations $[I^\cdot][I']/[I_2] = K_1$ and $[I^\cdot]\,[OH']/[HIO] = K_3$ we find,

$$K_1K_w/K_3 = [HIO][H^\cdot][I']/[I_2],$$

the value of which is 3×10^{-13} (Bray, *J. Amer. Chem. Soc.*, **1910**, **32**, 932). $K_1K_w/K_3 \,.\, 1/[H^\cdot]$, therefore, is of the order 10^{-12}, and ignoring it compared with the value of K_1, we can write,

$$K_1 = 0{\cdot}97 \times 10^{-8} \text{ at } 25°.$$

By substituting Bray's value in the expression above, we obtain in addition,

$$K_3 = 3{\cdot}2 \times 10^{-10} \text{ at } 25°.$$

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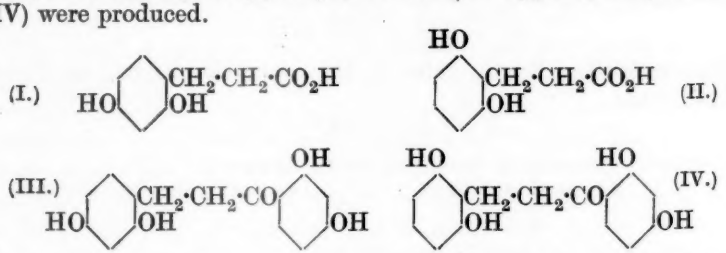
CXXIV.—*The Condensation of β-Chloro- and β-Ethylcarbonato-propionitriles with Resorcinol.*

By ERNEST CHAPMAN and HENRY STEPHEN.

UNTIL recently, the only limitation of Hoesch's method (*Ber.*, 1915, **48**, 1122) for the preparation of aromatic hydroxy-ketones was its inapplicability to phenolic compounds other than resorcinol,

orcinol, or phloroglucinol. Several cases are now on record, however, in which certain types of nitriles display exceptional behaviour. Cinnamonitrile and phloroglucinol in presence of hydrogen chloride yield 5 : 7-dihydroxy-4-phenyl-3 : 4-dihydrocoumarin (Fischer and Nouri, *Ber.*, 1917, **50**, 693; compare Stephen, J., 1920, **117**, 1531) instead of 2 : 4 : 6-trihydroxyphenyl styryl ketone, which would be expected, the reaction recalling the formation of 7-hydroxy-4-phenylcoumarin from benzacetodinitrile and resorcinol under similar conditions (von Meyer, *J. pr. Chem.*, **1903**, **67**, 342; Sonn, *Ber.*, 1918, **51**, 821). Acylacetonitriles of the type R·CO·CH_2·CN also yield coumarin derivatives (Sonn, *ibid.*, p. 1829; compare also Bargellini and Forli-Forti, *Gazzetta*, **1911**, **41**, 747). Again, condensation between β-chloropropionitrile and resorcinol takes place almost exclusively by loss of hydrogen chloride (Langley and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 2320), the final product being β-2 : 4-dihydroxyphenylpropionic acid (I) (dihydroumbelliferic acid).* The present authors had begun an investigation on similar lines two months before the publication of Langley and Adams's paper, the object being a synthesis of 7-hydroxychromanone analogous to that of 5-hydroxycoumaranone from chloroacetonitrile and resorcinol by Sonn (*Ber.*, 1917, **50**, 1262).

The first experiments indicated that the chromanone was not formed during the condensation and confirmed the results obtained by Langley and Adams (*loc. cit.*). Further investigation showed that, in addition to β-2 : 4-dihydroxyphenylpropionic acid, β-2 : 6-dihydroxyphenylpropionic acid (II) (which gave the corresponding lactone), 2 : 4-dihydroxyphenyl β-2 : 4-dihydroxyphenylethyl ketone (III), and 2 : 4-dihydroxyphenyl β-2 : 6-dihydroxyphenylethyl ketone (IV) were produced.



The formation of β-2 : 6-dihydroxyphenylpropionic acid (II) due to the substitution of a hydrogen atom in the vicinal position of resorcinol is remarkable. Apparently the only other instance of such substitution is the formation of 2 : 6-dihydroxybenzoic acid along with 2 : 4-dihydroxybenzoic acid from resorcinol and ammonium

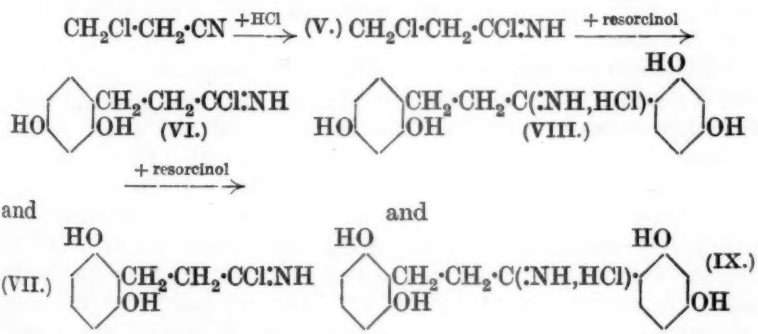
* Langley and Adams have also shown that γ-chlorobutyronitrile behaves similarly, yielding γ-2 : 4-dihydroxyphenylbutyric acid.

carbonate (Senhöfer and Brunner, *Wein Akad. Wiss.*, 1879, **80**, 504; Brunner, *Annalen*, 1906, **351**, 313; compare Zehenter, *ibid.*, 1881, 84, 341). Langley and Adams did not obtain the compounds (II), (III) and (IV). The ketones are interesting, since they are isomeric with phloretin and dihydrobutein.

The behaviour of β-chloropropionitrile in condensation with resorcinol offers an explanation of the cases cited above. The nitriles referred to are unsaturated and it is probable that the first reaction is the addition of hydrogen chloride, the resulting β-chloro-compound then reacting like β-chloropropionitrile. Langley and Adams also refer to this point and show that acrylonitrile behaves similarly to β-chloropropionitrile in condensation with resorcinol.

In view of the fact that Sonn and Falkenheim (*Ber.*, 1922, **55**, 2983) have synthesised fisetol from ethylcarbonatoacetonitrile and resorcinol, another attempt was made to synthesise 7-hydroxychromanone from β-ethylcarbonatopropionitrile and resorcinol. The results were in general the same as in the previous experiments with β-chloropropionitrile.

The experimental work has shown that three cases may be distinguished in condensations of the nitriles with resorcinol in presence of hydrogen chloride: (1) equimolecular quantities of β-chloropropionitrile and resorcinol gave the acid (I) (yield about 71% of the theoretical) and a small quantity of the acid (II); (2) β-chloropropionitrile (1 mol.) and an excess of resorcinol (4 mols.) gave the compounds (I), (II), (III) and (IV), the yield of (I) being smaller than in the previous case; (3) equimolecular quantities of β-ethylcarbonatopropionitrile and resorcinol gave all four compounds as in (2). The following scheme indicates the course of the reactions in cases (1) and (2):



The iminochlorides (VI) and (VII) on hydrolysis gave the acids (I) and (II), respectively. In case (2), interaction between a portion of each iminochloride and excess of resorcinol, following the usual

course of Hoesch's reaction, gave the ketimine hydrochlorides (VIII) and (IX) respectively, from which the corresponding ketones (III) and (IV) were obtained.

Case (3) also may be explained by the above scheme, but it is first necessary to consider the action of hydrogen chloride on β-ethylcarbonatopropionitrile. The experiments show that the following reactions take place:

$$EtO_2C{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CN \xrightarrow{HCl} (X.)\ EtO_2C{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CCl{:}NH \xrightarrow{HCl} CH_2Cl{\cdot}CH_2{\cdot}CCl{:}NH\ (V.) + EtOH + CO_2.$$

The alcohol formed was shared between the iminochlorides (X) and (V), giving a mixture of the hydrochlorides of β-ethylcarbonatopropioiminoethyl ether, $EtO_2C{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}C(OEt){:}NH,HCl$, and β-chloropropioiminoethyl ether, $CH_2Cl{\cdot}CH_2{\cdot}C(OEt){:}NH,HCl$. The composition of the mixture was determined by hydrolysis, which gave ethyl β-ethylcarbonatopropionate and ethyl β-chloropropionate. The same reactions evidently took place in case (3), because the same two esters were isolated. The formation of the above ethers diminished the concentration of β-chloropropioiminochloride (V), and the resorcinol being now in excess the condensation proceeded as in case (2).

Experimental.

β-*Chloropropionitrile.*—To a solution of 28 g. of ethylene cyanohydrin in 30 c.c. of chloroform cooled in ice and salt, 50 g. of thionyl chloride were added gradually with shaking. After an hour, the chloroform was evaporated and the residue of brown oil distilled under diminished pressure. The nitrile was obtained as a colourless liquid, b. p. 85—87°/20 mm., 173—174·5° at ordinary pressure (Henry, *Bull. Acad. roy. Belg.*, 1898, **35**, 360, gives b. p. 174—176°/752 mm.).

β-*Ethylcarbonatopropionitrile.*—Ethyl chloroformate (170 g.) was added during 2 hours with vigorous shaking to a solution of ethylene cyanohydrin (85 g.) in dry pyridine (220 g.) cooled with water. After 12 hours, the deep red solution was acidified with 130 c.c. of concentrated hydrochloric acid diluted with 500 c.c. of water, care being taken to avoid rise in temperature. A heavy oil separated which was dissolved in ether, dried, and, after removal of the solvent, fractionated under diminished pressure, 123 g. of the nitrile being obtained (yield 72%), b. p. 127—128°/15 mm., 206°/760 mm. [Found: C = 50·3, 50·2; H = 6·6, 6·3; N (Kjeldahl) = 9·7, 9·6. $C_6H_9O_3N$ requires C = 50·3; H = 6·3; N = 9·8%]. The nitrile was a colourless liquid which did not solidify at −20°; it was heavier than water, in which it was almost insoluble, and was readily hydro-

lysed by the action of acids and alkalis, the ethylcarbonato-group being decomposed simultaneously with the nitrile group.

Action of Hydrogen Chloride on β-Ethylcarbonatopropionitrile.—Dry hydrogen chloride was passed for 5 hours into a well-cooled solution of the nitrile (50 g.) in dry, alcohol-free ether (75 c.c.). After 12 hours, the addition of 125 c.c. of dry ether caused the separation of a white crystalline mass, which was washed several times with dry ether and dried over caustic potash. Yield 36 g. No suitable solvent could be found for crystallising the solid, which melted at 102—103° (decomp.). From the analytical results (Found: C = 40·9, 41·1; H = 7·5, 7·6; N = 6·7, 6·6; Cl = 22·9, 23·0) it appeared improbable that the solid was β-ethylcarbonatopropioiminochloride, $EtO_2C{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CCl{:}NH$ (Calc., C = 40·1; H = 5·6; N = 7·8; Cl = 19·8%). It was readily soluble in water giving a clear solution, slightly acid to litmus, which on warming deposited globules of oil. The solid evolved ethyl chloride a few degrees above its m. p., and gave ammonia on treatment with dilute sodium hydroxide solution. These properties are characteristic of the hydrochloride of an iminoethyl ether (compare Pinner and Klein, *Ber.*, 1877, **10**, 189).

The colourless oil which separated on warming an aqueous solution of the solid (25 g. in 30 c.c.) was dissolved and dried in ether. The neutral liquid (18 c.c.) remaining after removal of the solvent was separated into two fractions, b. p. 160—170° (3 c.c.) and 229—231° (10 c.c.). The former consisted of ethyl β-chloropropionate (b. p. 162—163°) (Found: C = 43·4; H = 6·6; Cl = 25·3. Calc., C = 43·9; H = 6·6; Cl = 26·0%); the latter was *ethyl β-ethylcarbonatopropionate* (Found: C = 50·7, 50·4; H = 7·5, 7·6. $C_8H_{14}O_5$ requires C = 50·5; H = 7·4%), a colourless neutral liquid, b. p. 230°, which is slowly hydrolysed by cold dilute sodium hydroxide solution.

It is therefore justifiable to conclude that the solid consisted of a mixture of the hydrochlorides of β-chloropropioiminoethyl ether and β-ethylcarbonatopropioiminoethyl ether, which on hydrolysis would give the above esters.

Condensation of Resorcinol and β-Chloropropionitrile.—(1) Using equimolecular quantities. The method and conditions employed were similar to those described by Langley and Adams (*loc. cit.*), but a higher yield was obtained (71%), 11 g. of resorcinol and 9 g. of the nitrile giving 13 g. of β-2 : 4-dihydroxyphenylpropionic acid, m. p. 165° (Found: C = 59·5; H = 5·5. Calc., C = 59·3; H = 5·5%). During the crystallisation of the crude acid from hot water a small quantity of β-2 : 6-dihydroxyphenylpropionic acid (see next section) separated first from solution. β-2 : 4-Dihydr-

oxyphenylpropionic acid is only slightly soluble in hot benzene or chloroform, but readily soluble in most other solvents. The aqueous solution gave an indigo-blue coloration with ferric chloride, and reduced ammoniacal silver nitrate in the cold and Fehling's solution on warming. Acetylation of the acid with acetic anhydride gave *7-acetoxy-3 : 4-dihydrocoumarin*, transparent prisms from alcohol, m. p. 111—111·5° (Found : C = 64·0; H = 4·9. $C_{11}H_{10}O_4$ requires C = 64·0; H = 4·9%). Hydrolysis of the coumarin with dilute hydrochloric acid gave the above acid. The latter on heating for 2 hours at 125—130° was converted into the lactone, *7-hydroxy-3 : 4-dihydrocoumarin* (dihydroumbelliferone), flat plates from toluene, m. p. 133—134° (Found : C = 66·0; H = 4·8. $C_9H_8O_3$ requires C = 65·9; H = 4·9%). Acetylation gave the acetyl compound described above.

(2) Using excess of resorcinol. A solution of 11·5 g. (1 mol.) of β-chloropropionitrile and 56 g. (4 mols.) of resorcinol in 200 c.c. of dry ether was cooled in ice and salt and saturated with hydrogen chloride. Zinc chloride was not used. The method of treating the reaction product was similar to that described in the next section, except that distillation with steam was omitted. Reference only need be made here to the compounds isolated, as these are described later, namely, β-2 : 4-dihydroxyphenylpropionic acid (12 g.), *β-2 : 6-dihydroxyphenylpropionic acid* (3·8 g.) and β-2 : 4- and β-2 : 6-*dihydroxyphenylethyl* 2 : 4-*dihydroxyphenyl ketones* (1·8 g. and 0·5 g. respectively).

Condensation of β-Ethylcarbonatopropionitrile and Resorcinol.—A rapid stream of hydrogen chloride was passed for 5 hours into a well-cooled solution of resorcinol (1·1 mols.; 60 g.) and the nitrile (1 mol.; 70 g.) in dry ether (200 c.c.). After remaining a week in an ice-chest, a red oil and a thick, crystalline deposit had formed, the quantity of which increased on the addition of 200 c.c. of dry ether. The ether layer was decanted from the oil and crystalline deposit, which were washed with a little ether and dissolved in 220 c.c. of water. From the red solution, on warming for a few minutes, an oil separated which was distilled with steam and proved to be a mixture of ethyl β-ethylcarbonatopropionate and ethyl β-chloropropionate (compare p. 889). The red solution remaining after steam distillation deposited a thick red oil mixed with a small amount of a pale yellow crystalline material. Both were removed with ether, and the aqueous solution was evaporated to dryness, leaving 23 g. of ammonium chloride containing no appreciable amount of organic matter. The ether extract was shaken with 600 c.c. of saturated aqueous sodium bicarbonate, and the aqueous layer (A), which had acquired a reddish-purple colour, was separated,

the ether layer being washed with a little water, dried, and the ether removed on the water-bath. A red oil remained, which gradually set to a crystalline mass (B) when cold. The aqueous layer (A) was acidified with hydrochloric acid, the colour changing from purple to yellow with deposition of a pale yellow, crystalline powder. This, crystallised from hot water with the addition of animal charcoal, gave 5 g. of β-2 : 6-dihydroxyphenylpropionic acid (see below). The filtrate was concentrated to a quarter of its bulk and extracted with ether; after removal of the solvent β-2 : 4-dihydroxyphenylpropionic acid (16·5 g.) remained.

β-2 : 6-*Dihydroxyphenylpropionic acid* crystallised from hot water in glistening, prismatic needles, which melted and decomposed at 174—176°, resolidified at 178°, and melted again at 224—225° (Found : C = 58·9, 59·4; H = 5·4, 5·6. $C_9H_{10}O_4$ requires C = 59·3; H = 5·5%). A solution of the acid in alcohol gave a red coloration with ferric chloride which distinguished it from the isomeric acid. In other respects, it resembled the latter. On fusion at 190° for ½ hour, the corresponding lactone, *5-hydroxy-3 : 4-dihydrocoumarin*, was obtained; it formed snow-white prisms, m. p. 224—225°, from alcohol after treatment with charcoal (Found : C = 65·7; H = 5·1. $C_9H_8O_3$ requires C = 65·9; H = 4·9%). It is sparingly soluble in cold and moderately soluble in hot water, from which it crystallises unchanged. It differs from its isomeride in being slightly soluble in boiling toluene. It is insoluble in sodium bicarbonate solution, but soluble in cold dilute sodium hydroxide, and the lactone was recovered unchanged on acidifying the solution immediately. On warming, the alkaline solution became orange-coloured and after acidification the corresponding acid was precipitated. An alcoholic solution of the lactone gave a reddish-brown coloration with ferric chloride. The formation of the lactone was taken as conclusive evidence for the formula of the acid.

The crystalline mass (B) was stirred with 15 c.c. of water, the greater part dissolving, leaving a residue of fine yellow needles (6·5 g.). The filtrate from the latter was evaporated, leaving 22 g. of unchanged resorcinol. The yellow crystalline residue was extracted successively with 200, 200, and 250 c.c. of boiling water. The residue (1 g.) after the third extraction was 2 : 4-*dihydroxyphenyl* β-2 : 6-*dihydroxyphenylethyl ketone*, which on crystallising from alcohol with the addition of charcoal was obtained in fine white needles, m. p. 228—229° (Found : C = 65·5, 65·6; H = 5·2, 5·1. $C_{15}H_{14}O_5$ requires C = 65·7; H = 5·1%). There was insufficient material for the preparation of derivatives. The ketone was only slightly soluble in hot water, readily soluble in hot alcohol or acetic

acid, the alcoholic solution giving a reddish-brown coloration with ferric chloride. It dissolved in aqueous sodium hydroxide and was recovered unchanged after boiling and acidifying the red solution. This behaviour distinguished the ketone definitely from the lactone of β-2 : 6-dihydroxyphenylpropionic acid. A mixture of the two melted at 208—211°.

2 : 4-*Dihydroxyphenyl* β-2 : 4-*dihydroxyphenylethyl ketone* was deposited from the first of the aqueous extracts * above in diamond-shaped plates (4 g.), which lost 2 mols. of water at 100°, the anhydrous compound melting at 186° (Found: in material dried in a vacuum for 30 hours or 4 days, loss at 110° = 11·6, 11·7: in the anhydrous substance, C = 65·8, 65·5; H = 5·2, 5·1. $C_{15}H_{14}O_5,2H_2O$ requires H_2O = 11·6%. $C_{15}H_{14}O_5$ requires C = 65·7; H = 5·1%). The ketone, unlike the isomeride above, was readily soluble in hot water, and insoluble in benzene, ligroin, or chloroform. An alcoholic solution gave a reddish-brown coloration with ferric chloride. The *phenylhydrazone* was obtained by warming the anhydrous ketone (0·9 g.) with excess of phenylhydrazine (1·25 g.), and after crystallisation from alcohol was obtained in pale brown needles, m. p. 214—215° (Found: N = 7·9, 7·8. $C_{21}H_{20}O_4N_2$ requires N = 7·7%).

In conclusion, one of us (E. C.) desires to express his thanks to the Trustees of the Sir Clement Royds Memorial Scholarship, during the tenure of which a portion of the above work was completed.

THE UNIVERSITY OF MANCHESTER. [*Received, February 24th*, 1925.]

CXXV.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part X. The Action of Hydrazine Hydrate on the Halogen Derivatives of α-Nitro-fatty Acids.*

By ALEXANDER KILLEN MACBETH and DAVID TRAILL.

THE investigations (J., 1922, **121**, 892, and subsequent papers) on the influence of various groups on the reactivity of halogen compounds towards reducing agents—notably hydrazine hydrate—have been supplemented by a study of derivatives of representative α-nitro-fatty acids. Substances containing the structures ·CO·CHX·CO·, ·CO·CX_2·CO·, ·CO·CHX·CO_2Et, ·CO·CX_2·CO_2Et, EtO_2C·CRX·CO_2Et, EtO_2C·CX_2·CO_2Et (where X represents a halogen atom) have already been examined, and it seemed of

* The second extract deposited a small quantity of the previous ketone.

interest to prepare compounds of the types $O_2N{\cdot}CRX{\cdot}CO_2Et$, $O_2N{\cdot}CX_2{\cdot}CO_2Et$ for comparison.

Two main views have been advanced to account for the reactivity of the halogen atoms in compounds of the types we have examined, one based on the tautomeric hydrogen hypothesis (Burton and Kenner, J., 1922, **121**, 489: see also Thole and Thorpe, J., 1911, **99**, 2183; Norris and Thorpe, J., 1921, **119**, 1203), the other on the polarity of the oxygen atoms. Opinions have been expressed (Robinson, *Ann. Reports*, 1922, **19**, 102; Allsop and Kenner, J., 1923, **123**, 2296) that both factors may in different cases contribute to the observed reactivities, and apparently contradictory observations may be accounted for on such grounds. The chief outstanding cases in which direct polarity effects leading to a "positive" halogen cannot be traced are the tetrahalogen derivatives of methane. Nef (*Annalen*, 1899, **308**, 329) and Gustavson (*ibid.*, 1874, **172**, 173) have shown that such substances are converted into trihalogenomethanes by a variety of alkaline reducing agents, and further examples of similar effects have been recorded by Griffith and Hunter (J., 1924, **125**, 463). We now find that the action of hydrazine hydrate on tetrabromomethane results in reduction, the removal of one of the bromine atoms, and the liberation of the corresponding volume of nitrogen. The consideration of steric effects (Chattaway and Harrison, J., 1916, **109**, 171) would appear to furnish the most satisfactory explanation of the lability of the halogen atom in these cases.

The present results support those obtained in our previous work, hydrazine hydrate displaying, in the case of the α-nitro-fatty acids now examined, its capacity of differentiating between the reactivities of chlorine and bromine atoms in compounds of precisely similar structure.

The reactivity of chlorotrinitromethane is much less than that of the corresponding bromo-compound, although reduction occurs in both cases (Macbeth and Pratt, J., 1921, **119**, 1356). More striking effects are found in the case of certain diketones, no reduction occurring in such derivatives as 4 : 4-dichloro-1 : 1-dimethyl-*cyclo*hexane-3 : 5-dione and *cyclo*hexane*spiro*-4 : 4-dichloro*cyclo*hexane-3 : 5-dione, whereas nitrogen is readily liberated when the corresponding dibromo- and chlorobromo-compounds are treated with hydrazine hydrate, one bromine atom being removed by the reducing agent in each case. In agreement with these observations, all the chloro-derivatives of the α-nitro-fatty acids examined are unacted upon by hydrazine hydrate, whereas bromine is readily removed from the corresponding bromo- and chlorobromo-compounds.

These effects seem to us to be best explained on a polarity basis. It might be urged that the desire to acquire a tautomeric hydrogen atom, or the operation of steric influences, may equally well be the factor governing the lability of the halogen atom in such compounds as dibromonitroacetic, bromonitropropionic and bromonitrobutyric esters. But such an explanation is considerably weakened when it is seen that the corresponding chloro-compounds are not reactive under the same experimental conditions: and it is still more difficult to reconcile the reactivity of bromonitroacetic ester with views other than those developed on polarity considerations. The behaviour of the latter compound falls into line with the reactivities of the monohalogen derivatives of malonic and acetoacetic esters; and since these compounds already possess a hydrogen atom attached to the α-carbon atom, the tautomeric hydrogen hypothesis is inapplicable, and the development of spatial effects is not to be expected.

The properties of the nitro-fatty acids would appear to suggest that the influence of the nitro-group in inducing reactivity of the halogen atom is less than that of a ketonic or carbethoxyl group, as will be seen in the following examples.

Halogen reduced by hydrazine.	Halogen not reduced.
$R\cdot CO\cdot CHCl\cdot CO_2Et$	
$R\cdot CO\cdot CRCl\cdot CO_2Et$	
$R\cdot CO\cdot CCl_2\cdot CO_2Et$	$O_2N\cdot CHCl\cdot CO_2Et$
$EtO_2C\cdot CHCl\cdot CO_2Et$	$O_2N\cdot CRCl\cdot CO_2Et$
$EtO_2C\cdot CRCl\cdot CO_2Et$	$O_2N\cdot CCl_2\cdot CO_2Et$
$EtO_2C\cdot CCl_2\cdot CO_2Et$	

Support for this view is found on comparing the properties of the bromine atom in ethyl bromonitroacetate and bromodinitromethane: the former is readily reduced by hydrazine at the ordinary temperature, whereas the latter is unaffected (Macbeth and Pratt, *loc. cit.*).

EXPERIMENTAL.

The hydrazine reactions were in all cases carried out with a 50% solution of hydrazine hydrate in a Van Slyke nitrometer.

Tetrabromomethane was prepared by Ponzio's method (*Atti R. Accad. Sci. Torino*, 1906, 41, 415). In alcoholic solution it reacted vigorously with hydrazine hydrate, one bromine atom being removed and the corresponding volume of nitrogen liberated. 0·3305 Gram of tetrabromomethane liberated 11·3 c.c. of nitrogen at 14·5° and 756 mm., which corresponds with a 96% reduction.

Nitroacetic Acid Series.

Ethyl Monochloronitroacetate.—Dry ammonia gas was passed into an ethereal solution of ethyl nitroacetate (prepared by Bouveault

and Wahl's method, *Bull. Soc. chim.*, 1904, **31**, 851) and the ammonio-derivative so obtained was chlorinated and brominated as described below.

The chloro-ester was best obtained by passing a slow stream of chlorine into an aqueous solution of the ammonio-derivative for 1 hour. The heavy yellow oil which had separated was extracted with ether, washed with a dilute solution of sodium thiosulphate and with water, dried over anhydrous sodium sulphate, and, after removal of the solvent, distilled under reduced pressure. Ethyl monochloroacetate collected as a main fraction, b. p. 77°/8 mm., n_D 1·4412 (Found: Cl, 21·2. Calc., Cl, 21·2%). The ester was practically unacted upon by hydrazine hydrate, traces only of nitrogen being liberated after upwards of ½ hour.

The *ammonio-derivative of ethyl monochloronitroacetate* was prepared by the action of dry ammonia gas on an ethereal solution of the chloro-ester. It separated as a white, flaky solid, but gradually changed to a compact, yellow precipitate. The compound is fairly stable, but reddens somewhat on exposure to air. It crystallises in long, white needles, m. p. 114—115°, from alcohol. Crystallisation presents a curious appearance under the microscope; in the thicker parts a mosaic structure forms, with peculiar interference in growth: in other parts rosettes form (Found: Cl, 19·2. $C_4H_9O_4N_2Cl$ requires Cl, 19·3%).

Ethyl dichloronitroacetate gradually separated when a slow stream of chlorine was passed into an aqueous solution of the preceding compound, and was treated as described in the case of the monochloro-compound. It has b. p. 72°/8 mm., n_D 1·4430 (Found: Cl, 35·1. $C_4H_5O_4NCl_2$ requires Cl, 35·15%).

As in the case of the monochloro-ester there is practically no reaction with hydrazine hydrate.

Ethyl Bromonitroacetate.—The ammonio-derivative of nitroacetic ester was gradually added, with occasional shaking, to a solution of bromine (1 mol.) in carbon disulphide. Water was added to dissolve the precipitated ammonium bromide, and the carbon disulphide was thereafter successively washed with a dilute solution of sodium thiosulphate and water. After drying and removal of the solvent, the residual oil was distilled under reduced pressure, when the bromo-ester collected as a main fraction, b. p. 105°/10 mm., $n_D^{16°}$ 1·4798 (Found: Br, 37·6. $C_4H_6O_4NBr$ requires Br, 37·7%).

The ester reacts readily with hydrazine hydrate, nitrogen being liberated and the halogen atom removed by reduction. 2·12 Grams of the bromo-ester were dissolved in 25 c.c. of alcohol, and 5 c.c. of this solution liberated 12·2 c.c. N_2 at 13·5° and 741·5 mm., which corresponds with complete reduction of the bromo-ester.

The *ammonio-derivative of ethyl bromonitroacetate*, prepared as in the preceding cases, crystallised from alcohol in long, colourless needles, m. p. 134° (decomp.) (Found: NH_3, 7·7. $C_4H_9O_4N_2Br$ requires NH_3, 7·8%).

Ethyl dibromonitroacetate, prepared from the preceding compound by bromination in carbon disulphide solution as previously described, was a colourless liquid, b. p. 97·4°/6 mm., n_D 1·4985 (Found: Br, 54·8. $C_4H_5O_4NBr_2$ requires Br, 55·0%).

The ester reacts vigorously with hydrazine hydrate. 1·455 Grams were dissolved in 25 c.c. of alcohol, and 5 c.c. of the solution liberated 13 c.c. N_2 at 14·5° and 747 mm., which corresponds with 100% reduction of the dibromo-ester. 5—6 C.c. of the gas were liberated almost immediately, the residual volume collecting in about 5 minutes.

Ethyl chlorobromonitroacetate, prepared by the bromination in carbon disulphide solution of the ammonio-derivative of ethyl chloronitroacetate, was a colourless oil, b. p. 89°/11 mm., n_D 1·4663 (0·1572 of the ester gave 0·212 of silver halides: calc. for $C_4H_5O_4NClBr$, 0·218).

The ester reacts with hydrazine hydrate, the reduction removing only the bromine atom. 1·2325 Grams were dissolved in 25 c.c. of alcohol, and 5 c.c. of this solution liberated 9·6 c.c. N_2 at 14° and 765 mm., which corresponds with about 83% removal of the bromine atom.

Nitropropionic Acid Series.

The ammonio-derivative of ethyl nitropropionate was prepared by the action of alcoholic ammonia on ethyl nitro*iso*succinate. Some difficulty was experienced at first in obtaining a good yield of ethyl nitro*iso*succinate by Steinkopf and Supan's method (*Ber.*, 1910, **43**, 3245), but this was probably due to imperfect decomposition of the acetic anhydride in the later stages, and in subsequent experiments better yields were obtained when the mixture after reaction was shaken by mechanical means for upwards of an hour with 2 litres of cold water.

Attempts to prepare ethyl nitropropionate by the direct nitration of ethyl methylacetoacetate in acetic anhydride gave very low yields of the ester.

Ethyl-α-chloronitropropionate was obtained in good yield by passing a stream of chlorine into an aqueous solution of the ammonio-derivative of the nitro-ester; after about 30 minutes, most of it separated as a pale green oil. After the usual treatment the ester was obtained as a colourless oil, b. p. 80°/9 mm., n_D 1·4301 (Found: Cl, 19·1. $C_5H_8O_4NCl$ requires Cl, 19·55%). The ester is practically unacted upon by hydrazine hydrate,

only a small volume of nitrogen being liberated at the laboratory temperature.

Ethyl α-bromonitropropionate, prepared by bromination of the ammonio-derivative of the nitro-ester by a precisely similar method to those already described, was a clear, colourless liquid, b. p. 88°/20 mm., n_D 1·4535 (Found: Br, 35·4. $C_5H_8O_4NBr$ requires Br, 35·6%).

The ester reacts very vigorously with hydrazine hydrate at the ordinary temperature, the nitrogen being all liberated in about 30 seconds. 1·130 Grams of the ester were dissolved in 25 c.c. of alcohol, and 5 c.c. of this solution liberated 11·8 c.c. N_2 at 16° and 764 mm., which corresponds with complete removal of the halogen atom.

Hydrazine Derivative of Ethyl α-Nitropropionate.—During the hydrazine reactions described above, a white solid collected in the reaction vessel. It crystallised from alcohol in long, white, silky needles, m. p. 120°, and proved to be the hydrazine derivative of ethyl α-nitropropionate (Found: N, 23·7. $C_5H_{13}O_4N_3$ requires N, 23·5%).

Rimini's method (*Atti R. Acad. Lincei*, 1906, **15**, ii, 320) for the estimation of hydrazine in a hydrazine salt was modified for use in a Van Slyke nitrometer. A weighed quantity of the hydrazine derivative was washed into the reaction bulb with water, and a measured volume of potassium iodate added. On addition of a known volume of potassium hydroxide solution a vigorous reaction occurred with liberation of nitrogen (Found: N_2H_4, 17·9. $C_5H_{13}O_4N_3$ requires N_2H_4, 17·9%).

Nitrobutyric Acid Series.

Ethyl α-Chloronitrobutyrate.—Ethyl nitrobutyrate was prepared from ethyl ethylacetoacetate by Schmidt and Widman's method (*Ber.*, 1909, **42**, 1895).

The chloronitro-ester was obtained in good yield by chlorination of the freshly prepared ammonio-derivative of the nitro-ester. It is a colourless oil, b. p. 77—79°/6 mm., n_D 1·4338 (Found: Cl, 18·1. $C_6H_{10}O_4NCl$ requires Cl, 18·2%).

As in the case of the other chloro-compounds the reduction of the ester by hydrazine hydrate is negligible.

Ethyl α-bromonitrobutyrate, prepared by bromination of the ammonio-derivative of the nitro-ester in carbon disulphide, had b. p. 83—84°/9 mm., n_D 1·4990 (Found: Br, 33·1. $C_6H_{10}O_4NBr$ requires Br, 33·3%).

The ester reacts vigorously with hydrazine hydrate, the reduction being complete in about 30 seconds. 5 C.c. of an alcoholic solution

containing 4·8% of the bromonitro-ester liberated 11·6 c.c. N_2 at 16° and 767 mm., which corresponds with complete removal of the halogen atom.

We are indebted to the Department of Scientific and Industrial Research for a grant which enabled one of us (D. T.) to participate in the work.

THE UNIVERSITY, DURHAM.
THE UNIVERSITY, ST. ANDREWS. [*Received, January 31st*, 1925.]

CXXVI.—*The Chemistry of Petroleum. Part I. The Occurrence of Compounds of Sulphur in the Light Distillate from the Crude Oil of Maidan-i-Naftun.*

By STANLEY FRANCIS BIRCH and WOODFORD STANLEY GOWAN PLUCKNETT NORRIS.

THE sulphur that is found in the distillates from all crude petroleums is present as free sulphur, or as sulphur compounds having a highly objectionable odour. The removal of these compounds is of the greatest importance to the refiner, who until recently had no clue as to their identity and who has removed them by purely empirical methods.

The isolation and identification are here described of some of the sulphur compounds present in the first 36% (by volume) of the distillate from crude Persian petroleum, *i.e.*, the fraction from which petrol and kerosene are obtained.

The crude oil itself is obtained from the wells at Maidan-i-Naftun, which is about 140 miles north-north-east of Mohammerah, in south-east Persia. As it issues from the wells it is accompanied by much gas, which consists chiefly of paraffin hydrocarbons together with a large proportion of hydrogen sulphide. The quantity of the latter constituent naturally varies with the pressure of the gas–liquid system from which the sample is taken; in fact, after keeping for some time at atmospheric pressure, the crude oil retains so little hydrogen sulphide that it has only a faint, somewhat sweet odour.

In marked contrast with the crude oil, the sulphur compounds in the distillates have, as stated above, a highly objectionable odour; this alone, we think, is sufficient proof that they are not present as such in the original petroleum, but are formed by decomposition, a conclusion borne out by the behaviour of the crude oil on distillation. When the temperature of the oil reaches about 120°,

elementary sulphur appears in the distillate. Moreover the total content of free and combined sulphur of the earlier fractions may be reduced by distilling the oil in such a way that the temperature is kept as low as possible, for example, by using an ample current of steam. This confirms the hypothesis that the appearance of sulphur compounds in the distillate is preceded by a thermal decomposition in the liquid phase.

The sulphur compounds in the 36% distillate are of two kinds, acidic and neutral. The first class includes hydrogen sulphide and (*vide infra*) mercaptans. The compounds of the second class react with mercuric chloride, but we have not yet examined the additive compound in any detail. Since Waterman and Heimel (*Chem. Weekblad*, 1924, **21**, 374) have reported the absence of thiophen from the distillates from Persian oil, the neutral compounds responsible for the mercuric chloride reaction must presumably be organic sulphides. In the absence of evidence to the contrary, organic disulphides, or carbon disulphide, may likewise be present. The distillate also contains elementary sulphur. In the present research we have investigated the acidic, sulphur-containing constituents of the 36% distillate, because this material is treated with sodium hydroxide solution in the normal course of refining, and a supply of " spent soda solution " was therefore available.

The organic sulphur compounds are readily isolated from " spent soda " by distillation, during which progressive hydrolysis of the sodium mercaptides occurs. This operation does not cause the liberation of hydrogen sulphide. The mercaptans are, in fact, very much weaker acids even than hydrogen sulphide. Thus they are only partly removed from solution in a hydrocarbon by shaking with sodium hydroxide solution, whereas hydrogen sulphide, in an equivalent quantity, is completely extracted. Moreover, apart from distillation or acidification, the mercaptans may be partly isolated from an alkaline solution by dilution, or by shaking with petroleum. This point is of importance in refinery practice, both because the mercaptans are incompletely extracted from petroleum distillates by washing with sodium hydroxide solution, and because the " spent soda " may be partly revivified by boiling.

The mercaptans were isolated from the crude mixture of sulphur compounds by shaking with 50% potassium hydroxide solution and acidifying the aqueous liquid. The material thus obtained was fractionally distilled, yielding about 55—60% of *iso*propyl mercaptan, 18% of *iso*butyl mercaptan, and 9% of fractions of low boiling point which appeared to consist of ethyl mercaptan. Intermediate fractions and the high-boiling residue accounted for the remainder.

We believe ourselves correct in stating that mercaptans have not hitherto been isolated from petroleum. References to these compounds are, of course, scattered throughout the technical literature;* but an actual separation seems never to have been accomplished.

Owing to its presence in so large a proportion of the total, the identification of *iso*propyl mercaptan, the first of the sulphur compounds which we succeeded in isolating, presented no special difficulty. The fraction of b. p. 56—58° was analysed and various indubitable derivatives of *iso*propyl mercaptan were prepared from it.

The second fraction, b. p. 86—88°, was identified in a similar manner as *iso*butyl mercaptan.

Owing to the small quantity (9%) obtained of the fraction which appeared to be ethyl mercaptan, a pure specimen of this substance could not be isolated. Indications of its presence were nevertheless obtained (see p. 903).

Analysis of the mercurichloride prepared from the fraction of highest boiling point seemed to indicate the presence of a higher mercaptan. By analogy with the lower homologues present, *iso*amyl mercaptan would appear the most likely. Certainly, apart from ethyl mercaptan, normal mercaptans do not appear to be present in the 36% distillate from Persian petroleum; we seem, in fact, to have a further example of the prevalence, in compounds from natural sources, of the *gem*-dialkyl grouping. It will of course be realised that the structure of the mercaptans found in the distillate is determined by the constitution of the more complex molecule, or molecules, from which they are eliminated during distillation. Without attempting to base any broad generalisation upon the somewhat meagre facts so far elicited, we may suggest that possibly that part of the parent molecule which is eliminated as a mercaptan has originally been formed by the addition of hydrogen sulphide to an ethylenic bond. This would tend to produce a branched chain rather than a normal configuration.

The mercaptans isolated were actually obtained from "spent soda." There was, therefore, an apparent possibility that the normal isomerides, although present in the petroleum distillates, might escape extraction during the soda-washing process owing to their extremely feeble acidity. This explanation of the absence of normal mercaptans from "spent soda" is not correct, however,

* For example, Engler-Höfer ("Das Erdöl," I, p. 477) quotes a statement by Kwjatkowsky that mercaptans are present in Baku petroleum (*Anleitung z. Verarb. d. Naphta*, 12, 1904, aus Höfer, *Erdöl u. s. Verw.*, 2 Aufl., 82).

Incidentally it should be noted that no mention is made by Engler-Höfer of the presence in petroleum of disulphides.

for in a series of comparative experiments, in which solutions containing equivalent quantities of various mercaptans were extracted by means of a given volume of 5% sodium hydroxide solution, it was found that the normal mercaptans were slightly stronger acids than their respective isomerides. Incidentally, the decrease in acidity with increase in molecular weight was very marked.

The portion of the sulphur compounds from "spent soda" which was insoluble in 50% potassium hydroxide solution consisted of organic disulphides, together with traces of hydrocarbons. It is evident that these compounds, being neutral, could not have been extracted from the petroleum distillate by means of sodium hydroxide solution. They must, in fact, have been formed in the "spent soda" subsequent to the process of extraction. Although at first a complete explanation of their production was not forthcoming, a clue was found in an observation of Böttger (*Annalen*, 1884, **223**, 348); he showed that sodium ethylmercaptide and sulphur, when heated at 100° in presence of ethyl alcohol, give diethyl disulphide and sodium polysulphide. Such drastic conditions are not, however, necessary to bring about the change, since Holmberg (*Annalen*, 1908, **359**, 81) has found that alkali mercaptides react in aqueous solution with free sulphur or an alkali polysulphide to give organic disulphides at the ordinary temperature, an observation which we have confirmed. Wendt and Diggs (*Ind. Eng. Chem.*, 1924, **16**, 1113) are apparently unaware of Holmberg's work on the subject; they state that diethyl disulphide is formed by the action of sulphur on ethyl mercaptan in petroleum solution. The 36% distillate from Persian petroleum certainly contains free sulphur, which might be to some extent the cause of the production of disulphides. The latter would then, however, be found in the petroleum, from which they could not be extracted by sodium hydroxide solution. But actually it is from the "spent soda" that they have been isolated; it is clear, therefore, that the formation of the disulphides must occur in the aqueous layer subsequent to extraction. Moreover, since the "spent soda," previous to being distilled, is free from any visible quantity of oily material, it seems certain that the disulphides are actually formed during the process of distillation. It is probable that the agent responsible for the oxidation is sodium polysulphide, which is invariably present, and imparts to the "spent soda" a pronounced yellow colour. The probability of this explanation has been greatly increased by the observation that, although a moderate increase in temperature does not appreciably affect the velocity with which sodium polysulphide oxidises mercaptans, heating the reaction mix-

ture to its boiling temperature very greatly hastens the production of disulphides. The total quantity of hydrocarbons present as impurity in the mixed disulphides is comparatively small, and we think this material consists simply of traces of the original petroleum distillate, carried mechanically in the spent soda.

The ease with which mercaptans are oxidised to give disulphides is somewhat surprising; the conversion may actually be brought about by passing oxygen, or air, into an aqueous solution of a sodium mercaptide. This result appears the more striking when the comparatively low solubility of oxygen in aqueous solutions is remembered.

The disulphides which have actually been isolated are diethyl disulphide, di*iso*propyl disulphide, and di*iso*butyl disulphide. Appropriate fractions were obtained by distillation, and then examined separately, but owing to the presence of hydrocarbons in these fractions, it was necessary to reduce each fraction to the corresponding mercaptan by means of zinc dust and glacial acetic acid. The mercaptans so obtained were then converted into solid derivatives and analysed or otherwise characterised in this form.

In subsequent researches it is hoped to deal with the sulphur compounds present in the 36% distillate which are not acidic but react with mercuric chloride, and also with the less volatile organic derivatives of sulphur which are present in the heavier distillates from crude Persian petroleum.

Experimental.

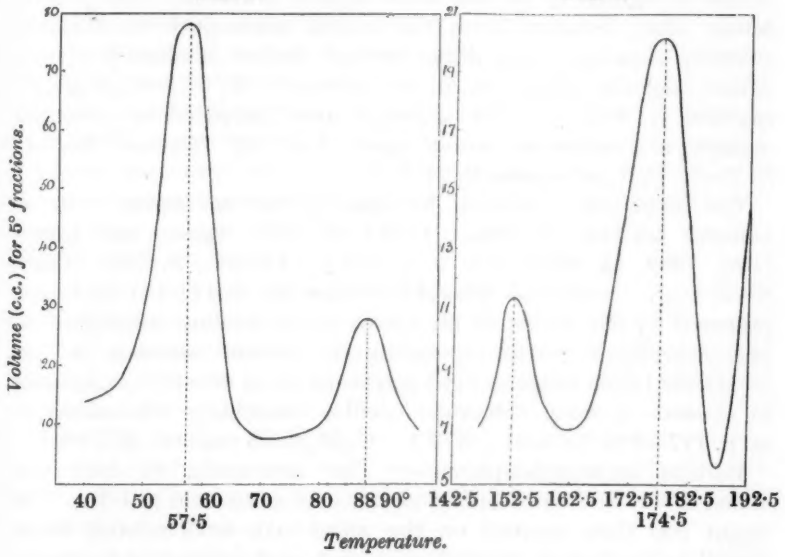
Isolation of the Organic Sulphur Compounds from "Spent Soda."—Spent soda (3 galls.), which was quite clear and apparently free from oil, was distilled during 5 hours from a 4-gallon iron drum, until oily drops could no longer be seen condensing. Great care was necessary to avoid liquid being carried over by frothing and to ensure complete condensation of the distillate, particularly at the commencement of the experiment. The yield from 40 gallons of spent soda was 720 c.c. of sulphur compounds. This material was exhaustively extracted with 50% potassium hydroxide solution, and the insoluble portion separated.

Isolation of Mercaptans.—The potassium hydroxide solution was extracted once with a small volume of ether to remove any traces of insoluble oil, diluted, and acidified with sulphuric acid, care being taken to prevent the temperature rising above 30°. The oil which separated was distilled with steam, and dried over calcium chloride, about 350 c.c. being obtained. This material was fractionally distilled, using a 24-inch Hempel column, 5°-fractions being collected. After two distillations, the curve shown in Fig. 1 was obtained,

in which, for successive fractions, the volume was plotted against the final boiling point. Pronounced peaks occur at 57·5° and 88°, corresponding with the respective boiling points of *iso*propyl and *iso*butyl mercaptans.

After two distillations, approximately 18% of the total mixed mercaptans was obtained between 36° and 50°. Further fractionation gave a portion, b. p. 36—38°, apparently consisting of ethyl mercaptan; the quantity was so small that further distillation was impossible. It was therefore converted into the solid phenylcarbimide additive compound, but even from this a specimen of the

FIG. 1. FIG. 2.



ethyl derivative free from a higher homologue could not be isolated. Nevertheless the presence of ethyl mercaptan was indicated by analysis of one of the intermediate fractions, b. p. 46—47° (Found: S, 44·8. C_3H_8S requires S, 42·1; C_2H_6S requires S, 51·6%). Moreover, the presence of ethyl mercaptan in the original spirit is quite certain, since a peak fraction consisting of diethyl disulphide was obtained during the examination of the mixed disulphides (*vide infra*).

The separation of mercaptans by distillation even of comparatively large quantities is a surprisingly difficult operation.

The fractions, b. p.'s 50—55°, 55—60°, and 60—65°, consisted almost entirely of *iso*propyl mercaptan. After several further distillations, a fraction, b. p. 56—58°, was obtained which was

identified as *iso*propyl mercaptan (Found: S, 42·1; SH, by titration, 42·9. Calc., S, 42·1; SH, 43·4%). The crystalline derivatives were in all cases identical with those prepared from a genuine specimen of the synthetic mercaptan.

The *mercurichloride*, obtained in boiling methyl-alcoholic solution, crystallises in very insoluble plates melting above 300° (Found: Hg, 64·2, 64·6. C_3H_7ClSHg requires Hg, 64·4%).

The action of moist, freshly prepared mercuric oxide on *iso*propyl mercaptan gives the chlorine-free *derivative*, $C_3H_7{\cdot}S{\cdot}Hg{\cdot}S{\cdot}C_3H_7$; it separates from dilute methyl alcohol in felted needles, m. p. 65° (Found: Hg, 56·9. $C_6H_{14}S_2Hg$ requires Hg, 57·1%). This compound is soluble in all the usual organic solvents. The p-*nitrobenzyl ether*, prepared from the sodium mercaptide in alcoholic solution, separates from dilute methyl alcohol in clusters of pale yellow, acicular prisms, m. p. 34° (Found: N, 6·7. $C_{10}H_{13}O_2NS$ requires N, 6·65%). The n-*propyl ether*, prepared in a similar manner, is a colourless, mobile liquid, b. p. 132°/760 mm. (Found: S, 27·2. $C_6H_{14}S$ requires S, 27·1%).

The disulphide, obtained by shaking the mercaptan with an aqueous solution of iodine, boiled at 174°; Spring and Legros (*Ber.*, 1882, **15**, 1940) give b. p. 174·5° (Found: S, 42·5. Calc., S, 42·7%). iso*Propyl phenylthiocarbamate*, $NHPh{\cdot}CO{\cdot}SPr^{\beta}$, was prepared by the action of an excess of the boiling mercaptan on phenylcarbimide. After spreading on porous porcelain it was crystallised from benzene–light petroleum (b. p. 40—60°), separating in clusters of long, colourless needles resembling wheatsheaves; m. p. 117—118° (Found: N, 7·4. $C_{10}H_{13}ONS$ requires N, 7·2%).*

Barium *iso*propylsulphonate: The mercaptan (6 c.c.) was added slowly and with cooling to 45 c.c. of nitric acid (*d* 1·3). The liquid was then warmed on the water-bath until nitrous fumes ceased to be evolved, diluted somewhat, and neutralised by means of an excess of barium carbonate. The filtered solution was mixed with sand and evaporated to dryness, and the residue, after being dried at 110°, exhaustively extracted with absolute ethyl alcohol. The soluble portion, consisting almost entirely of the barium sulphonate, was purified by dissolving in a small quantity of methyl alcohol (in which it is very soluble), adding ethyl alcohol, and boiling off the methyl alcohol. Barium *iso*propylsulphonate (Claus, *Ber.*, 1882, **5**, 660; 1875, **8**, 533) forms very small, white plates (Found: Ba, 36·0. Calc., Ba, 35·9%).

The fractions, b. p.'s 75—80°, 80—85°, and 85—90°, gave on

* n-*Propyl phenylthiocarbamate*, long, colourless needles, m. p. 84°, and n-*butyl phenylthiocarbamate*, felted, colourless needles, m. p. 73—74°, were also prepared for purposes of comparison.

distillation a fraction, b. p. 86—88°, which was identified as *iso*butyl mercaptan (Found : S, 35·8; SH, by titration, 36·2. Calc., S, 35·5; SH, 36·7%).

The *mercurichloride*, obtained in boiling methyl-alcoholic solution, crystallises in very insoluble, infusible plates (Found : Hg, 61·7, 61·9. C_4H_9ClSHg requires Hg, 61·8%).

Di*iso*butyl disulphide, prepared by shaking the mercaptan with an aqueous solution of iodine, boiled at 215°; Spring and Legros (*loc. cit.*) give b. p. 220° (Found : S, 36·1, 35·7. Calc., S, 36·0%).

Barium *iso*butylsulphonate (Mylius, *Ber.*, 1872, **5**, 978) was prepared in the manner described for the *iso*propyl derivative. It forms very small, white plates (Found : Ba, 33·4. Calc., Ba, 33·4%). iso*Butyl phenylthiocarbamate*, $NHPh{\cdot}CO{\cdot}S{\cdot}CH_2Pr^{\beta}$, prepared and purified as was the *iso*propyl ester, formed wheatsheaf clusters of long, colourless needles. The pure derivative, obtained from the synthetic mercaptan, melts at 111° (Found : N, 6·8. $C_{11}H_{15}ONS$ requires N, 6·7%). Owing to the presence of traces of the lower homologue, we were not able to obtain from our naturally occurring *iso*butyl mercaptan a sample of the phenylthiocarbamate having this melting point, our purest specimen melting at 102° (Found : N, 7·0%).

A search was made for higher mercaptans. The residue boiling above 95° gave on redistillation a fraction, b. p. 116—118°, from which the mercurichloride was prepared (Found : Hg, 60·2%). *iso*Amyl mercaptan boils at 120° [Nasini, *Ber.*, 1882, **15**, 2883, gives b. p. 116·6—118° (corr.)] and its mercurichloride, $C_5H_{11}ClSHg$, requires Hg, 59·2%. Since the mercurichloride of *iso*butyl mercaptan contains 61·8% of mercury, we consider this an indication of the possible occurrence of *iso*amyl mercaptan, the most probable of the amyl mercaptans.

Isolation of Disulphides.—The portion of the mixed sulphur compounds insoluble in 50% potassium hydroxide solution was washed well with water, dried over calcium chloride, and fractionally distilled, using a 6-inch Hempel column. During the first distillation, 10°-fractions were taken, but the second time 5°-fractions were collected and the volumes of successive fractions plotted against the relevant final boiling points (Fig. 2).

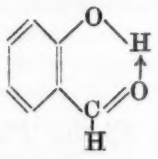
The curve shows two very distinct maxima, corresponding with the boiling points of, respectively, diethyl disulphide and di*iso*propyl disulphide. Following the second peak, the curve, after falling to a minimum at about 187°, rises again, thus giving a clear indication of the presence of a higher homologue, although a third maximum was not actually obtained. An examination of the high-boiling residue has shown this higher homologue to be the di*iso*butyl com-

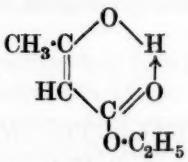
hydroxyl takes part. This is proved by comparing them with their meta- and para-isomerides: the ortho-compound invariably has a lower boiling point, and is more soluble in non-polar solvents like benzene and less soluble in water, than the other two. All these properties distinguish non-hydroxylic (non-associated) substances from hydroxylic, and we can conclude that in these ortho-compounds the hydroxyl group is not free, but forms part of a ring.

The object of this paper is to show, on similar grounds, that the same structure occurs in the enolic forms of β-diketones and β-keto-esters. We cannot here compare the possibly chelate enol with an isomeric enol in which the hydroxyl group is free, but only with its isomeric ketone; and since the association or polarity of ketones is small, we should not expect, even if the enol were wholly chelate, to find so sharp a contrast as we do with the phenols. If the enol does not form a ring, it will, as a hydroxylic compound, have a higher b. p. than the ketone, and will be more soluble in hydroxylic solvents and less in hydrocarbons. If the enol is wholly chelate, it will not be associated, and its b. p. should be lower than that of the ketone, and its solubility less in water and more in non-polar solvents.

K. H. Meyer and Schöller have shown (*Ber.*, 1920, **53**, 1410) that in the absence of a catalyst acetoacetic ester can be separated to a considerable extent into its two forms by fractional distillation, and that the enol comes over mainly in the first fractions of the distillate. Thus the enol is the more volatile. In water, the solubility of the enol at 0° is 0·5%, and that of the ketone 11%—more than twenty times as great, whilst in hexane we can calculate from the equilibrium that the enol is ten times as soluble as the ketone. Hence the enol is markedly less polar than the isomeric ketone, and cannot contain a free hydroxyl group: it must be a ring compound (II).

(I.)





(II.)

For other keto-enols, although the volatility data are lacking, the same solubility relations can be shown to hold. The effect of the solvent on the relative solubilities of the two forms can be calculated from the proportions at equilibrium; it is not necessary to know the solubilities themselves. The van't Hoff-Dimroth

relation may be put in the form $S_e/S_k = C_e/C_k \div G$, where S_e, S_k are the solubilities of enol and ketone in the solvent used, C_e, C_k their concentrations at equilibrium, and G is a constant for the tautomeric substance, independent of the solvent. It follows that for any given tautomeric substance the ratio of the solubilities is proportional to the ratio of the concentrations at equilibrium. The measurements of K. H. Meyer (*Ber.*, 1912, **45**, 2843; 1914, **47**, 826) have shown that for 11 keto-enols (to which others were added later) including acetoacetic ester, acetylacetone, benzoylacetone, dibenzoylmethane, and acetyl- and benzoyl-camphor, the solubility of the enol relative to that of the ketone is always in the order water <methyl alcohol<ethyl alcohol<benzene< hexane: that is, the enol always behaves as a non-hydroxylic and non-associated substance. We may conclude that the enolic modifications of all these substances are mainly if not wholly in the chelate form.

The ring of 6 atoms with two conjugate double links which occurs in these enols as well as in the ortho-substituted phenols mentioned above, is of enormously wide distribution: it is found in the majority of mordant dyes, in derivatives of alizarin, of *o*-hydroxyacetophenone, of *o*-quinone-oximes, of nitroso-β-naphthol, of the mono- and di-oximes of α-diketones, of hydroxypyrazolones, etc. One reason for this stability may be found by calculating the strain in the ring on the simple principles of Baeyer. Of the six angles in the ring, two are between single valencies, and have the usual value of $2\tan^{-1}\sqrt{2}$, or 109° 28′. The other four are angles between a single and a double link: this is the angle between the line joining the centre of a tetrahedron to one apex and that joining it to the middle point of an opposite edge: the value of this is $180° - \tan^{-1}\sqrt{2}$. Thus the sum of the six angles of the ring in an unstrained condition is $4(180° - \tan^{-1}\sqrt{2}) + 2 \times 2\tan^{-1}\sqrt{2} = 720°$, the exact sum of the angles of a plane hexagon. In other words, this form of ring * is entirely without strain. This conclusion is, of course, subject to the validity of certain simplifying assumptions; but it may be taken to be an approximation to the truth, and to afford an explanation of the remarkable stability of this type of ring.

DYSON PERRINS LABORATORY,
OXFORD.

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* The same remarks apply to the quinone ring.

identified as *iso*propyl mercaptan (Found: S, 42·1; SH, by titration, 42·9. Calc., S, 42·1; SH, 43·4%). The crystalline derivatives were in all cases identical with those prepared from a genuine specimen of the synthetic mercaptan.

The *mercurichloride*, obtained in boiling methyl-alcoholic solution, crystallises in very insoluble plates melting above 300° (Found: Hg, 64·2, 64·6. C_3H_7ClSHg requires Hg, 64·4%).

The action of moist, freshly prepared mercuric oxide on *iso*propyl mercaptan gives the chlorine-free *derivative*, $C_3H_7{\cdot}S{\cdot}Hg{\cdot}S{\cdot}C_3H_7$; it separates from dilute methyl alcohol in felted needles, m. p. 65° (Found: Hg, 56·9. $C_6H_{14}S_2Hg$ requires Hg, 57·1%). This compound is soluble in all the usual organic solvents. The *p-nitrobenzyl ether*, prepared from the sodium mercaptide in alcoholic solution, separates from dilute methyl alcohol in clusters of pale yellow, acicular prisms, m. p. 34° (Found: N, 6·7. $C_{10}H_{13}O_2NS$ requires N, 6·65%). The *n-propyl ether*, prepared in a similar manner, is a colourless, mobile liquid, b. p. 132°/760 mm. (Found: S, 27·2. $C_6H_{14}S$ requires S, 27·1%).

The disulphide, obtained by shaking the mercaptan with an aqueous solution of iodine, boiled at 174°; Spring and Legros (*Ber.*, 1882, **15**, 1940) give b. p. 174·5° (Found: S, 42·5. Calc., S, 42·7%). *iso*Propyl *phenylthiocarbamate*, $NHPh{\cdot}CO{\cdot}SPr^s$, was prepared by the action of an excess of the boiling mercaptan on phenylcarbimide. After spreading on porous porcelain it was crystallised from benzene–light petroleum (b. p. 40—60°), separating in clusters of long, colourless needles resembling wheatsheaves; m. p. 117—118° (Found: N, 7·4. $C_{10}H_{13}ONS$ requires N, 7·2%).*

Barium *iso*propylsulphonate: The mercaptan (6 c.c.) was added slowly and with cooling to 45 c.c. of nitric acid (*d* 1·3). The liquid was then warmed on the water-bath until nitrous fumes ceased to be evolved, diluted somewhat, and neutralised by means of an excess of barium carbonate. The filtered solution was mixed with sand and evaporated to dryness, and the residue, after being dried at 110°, exhaustively extracted with absolute ethyl alcohol. The soluble portion, consisting almost entirely of the barium sulphonate, was purified by dissolving in a small quantity of methyl alcohol (in which it is very soluble), adding ethyl alcohol, and boiling off the methyl alcohol. Barium *iso*propylsulphonate (Claus, *Ber.*, 1882, **5**, 660; 1875, **8**, 533) forms very small, white plates (Found: Ba, 36·0. Calc., Ba, 35·9%).

The fractions, b. p.'s 75—80°, 80—85°, and 85—90°, gave on

* n-*Propyl phenylthiocarbamate*, long, colourless needles, m. p. 84°, and n-*butyl phenylthiocarbamate*, felted, colourless needles, m. p. 73—74°, were also prepared for purposes of comparison.

distillation a fraction, b. p. 86—88°, which was identified as *iso*butyl mercaptan (Found : S, 35·8; SH, by titration, 36·2. Calc., S, 35·5; SH, 36·7%).

The *mercurichloride*, obtained in boiling methyl-alcoholic solution, crystallises in very insoluble, infusible plates (Found : Hg, 61·7, 61·9. C_4H_9ClSHg requires Hg, 61·8%).

Di*iso*butyl disulphide, prepared by shaking the mercaptan with an aqueous solution of iodine, boiled at 215°; Spring and Legros (*loc. cit.*) give b. p. 220° (Found : S, 36·1, 35·7. Calc., S, 36·0%).

Barium *iso*butylsulphonate (Mylius, *Ber.*, 1872, **5**, 978) was prepared in the manner described for the *iso*propyl derivative. It forms very small, white plates (Found : Ba, 33·4. Calc., Ba, 33·4%). iso*Butyl phenylthiocarbamate*, $NHPh{\cdot}CO{\cdot}S{\cdot}CH_2Pr^s$, prepared and purified as was the *iso*propyl ester, formed wheatsheaf clusters of long, colourless needles. The pure derivative, obtained from the synthetic mercaptan, melts at 111° (Found : N, 6·8. $C_{11}H_{15}ONS$ requires N, 6·7%). Owing to the presence of traces of the lower homologue, we were not able to obtain from our naturally occurring *iso*butyl mercaptan a sample of the phenylthiocarbamate having this melting point, our purest specimen melting at 102° (Found : N, 7·0%).

A search was made for higher mercaptans. The residue boiling above 95° gave on redistillation a fraction, b. p. 116—118°, from which the mercurichloride was prepared (Found : Hg, 60·2%). *iso*Amyl mercaptan boils at 120° [Nasini, *Ber.*, 1882, **15**, 2883, gives b. p. 116·6—118° (corr.)] and its mercurichloride, $C_5H_{11}ClSHg$, requires Hg, 59·2%. Since the mercurichloride of *iso*butyl mercaptan contains 61·8% of mercury, we consider this an indication of the possible occurrence of *iso*amyl mercaptan, the most probable of the amyl mercaptans.

Isolation of Disulphides.—The portion of the mixed sulphur compounds insoluble in 50% potassium hydroxide solution was washed well with water, dried over calcium chloride, and fractionally distilled, using a 6-inch Hempel column. During the first distillation, 10°-fractions were taken, but the second time 5°-fractions were collected and the volumes of successive fractions plotted against the relevant final boiling points (Fig. 2).

The curve shows two very distinct maxima, corresponding with the boiling points of, respectively, diethyl disulphide and di*iso*propyl disulphide. Following the second peak, the curve, after falling to a minimum at about 187°, rises again, thus giving a clear indication of the presence of a higher homologue, although a third maximum was not actually obtained. An examination of the high-boiling residue has shown this higher homologue to be the di*iso*butyl com-

pound. On redistillation of the fractions of final boiling points 147·5°, 152·5°, and 157·5°, the diethyl disulphide was largely concentrated into the 150—182° fraction. Reduction with zinc dust and boiling concentrated hydrochloric and glacial acetic acids, followed by distillation in steam, gave an oil, part of which was soluble in potassium hydroxide solution. This soluble portion was liberated by means of dilute sulphuric acid, separated, dried over anhydrous sodium sulphate, and distilled. The fraction boiling below 45° was converted into the mercurichloride (Found : Hg, 67·6. Calc. for C_2H_5ClSHg, Hg, 67·5%).

The fractions of final boiling points 172·5°, 177·5° and 182·5° were distilled, and a fraction, b. p. 173—175°, was collected. This was identified as di*iso*propyl disulphide by reducing it to *iso*propyl mercaptan. The material was treated under reflux for 48 hours with a large excess of zinc dust and boiling glacial acetic acid, the product distilled in steam, and the volatile oil dissolved in 50% potassium hydroxide. The alkaline solution was washed free from unreduced disulphide with ether, acidified, and the oil which separated washed with water, dried over calcium chloride and distilled. The fraction, b. p. 55—60°, was identified as *iso*propyl mercaptan by conversion into the *p*-nitrobenzyl ether, which melted at 34° and gave no depression of melting point when mixed with a genuine specimen.

The disulphide fraction, b. p. 210—230°, was shown to contain di*iso*butyl disulphide by a similar procedure. The product obtained on distillation was washed, dried, and fractionated, the portion boiling above 80° being converted into the mercurichloride (Found : Hg, 62·1. Calc. for C_4H_9ClSHg, Hg, 61·8%).

The Relative Acidities of Various Mercaptans and of Hydrogen Sulphide.—The following series of experiments indicates quite clearly the marked difference in the ease with which equivalent quantities of various mercaptans and of hydrogen sulphide are removed from solution in light petroleum by shaking with sodium hydroxide solution.

Solutions were prepared containing approximately 1/20 gram-mol. of the mercaptan in 250 c.c. of light petroleum (b. p. 60—80°); two portions of 25 c.c. of each solution were then removed and titrated iodometrically. The volumes (c.c.) of *N*/10-sodium thiosulphate equivalent to 25 c.c. of the light petroleum solution are given under *A* below. The remaining 200 c.c. were then shaken vigorously for 1 minute with 80 c.c. of 5% sodium hydroxide solution (*i.e.*, about 125% excess); after allowing to settle and removing the aqueous layer, 25 c.c. of the petroleum solution were removed and titrated as before. The equivalent quantity (c.c.) of

sodium thiosulphate solution is given under *B*; the figure under *C* refers to the percentage decrease in the concentration of mercaptan resulting from the sodium hydroxide treatment:

Mercaptan.	*A*.	*B*.	$C = 100(A - B)/A$.
Ethyl	33·54	0·97	97·1
n-Propyl	39·23	4·38	88·8
*iso*Propyl	39·92	5·10	87·2
n-Butyl	38·67	14·23	63·2
*iso*Butyl	41·78	15·55	62·8
*iso*Amyl	42·70	28·60	33·0

Apart from the obvious decrease in the acidity of the mercaptans with increasing molecular weight, it must be noted that *n*-propyl and *n*-butyl mercaptans are slightly more acidic than their branched-chain isomerides.

Hydrogen sulphide is a much stronger acid. A solution of this substance in light petroleum, approximately $1/5N$, was completely desulphurised by shaking with 5% sodium hydroxide solution in 125% excess. An interesting confirmation of this observation was found during the isolation of the organic sulphur compounds from "spent soda," a process depending, so far as the production of mercaptans is concerned, upon the progressive hydrolysis of the sodium mercaptides present; hydrogen sulphide was not eliminated at any stage of the operation. In fact, when the very light uncondensed vapours which were evolved were passed into an alcoholic solution of mercuric chloride, the precipitated mercurichloride was quite white, and therefore free from mercuric sulphide.

Our thanks are due to the Anglo-Persian Oil Company, Ltd., for permission to publish these results, to Professor J. F. Thorpe, C.B.E., F.R.S., for his kind interest in the progress of this research, to Dr. A. E. Dunstan, and to Dr. F. B. Thole for helpful suggestions received from time to time.

ANGLO-PERSIAN OIL CO., LTD.,
SUNBURY-ON-THAMES.

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CXXVII.—*The Structure of the Enolic Forms of β-Keto-esters and β-Diketones.*

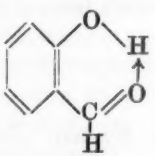
By NEVIL VINCENT SIDGWICK.

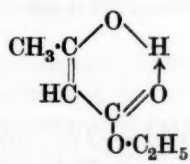
IT has been shown (Sidgwick and Callow, J., 1924, **125**, 527) that in certain ortho-substituted phenols (especially the nitro- and aldehydo-compounds) a chelate ring is formed (I) in which the

hydroxyl takes part. This is proved by comparing them with their meta- and para-isomerides: the ortho-compound invariably has a lower boiling point, and is more soluble in non-polar solvents like benzene and less soluble in water, than the other two. All these properties distinguish non-hydroxylic (non-associated) substances from hydroxylic, and we can conclude that in these ortho-compounds the hydroxyl group is not free, but forms part of a ring.

The object of this paper is to show, on similar grounds, that the same structure occurs in the enolic forms of β-diketones and β-keto-esters. We cannot here compare the possibly chelate enol with an isomeric enol in which the hydroxyl group is free, but only with its isomeric ketone; and since the association or polarity of ketones is small, we should not expect, even if the enol were wholly chelate, to find so sharp a contrast as we do with the phenols. If the enol does not form a ring, it will, as a hydroxylic compound, have a higher b. p. than the ketone, and will be more soluble in hydroxylic solvents and less in hydrocarbons. If the enol is wholly chelate, it will not be associated, and its b. p. should be lower than that of the ketone, and its solubility less in water and more in non-polar solvents.

K. H. Meyer and Schöller have shown (*Ber.*, 1920, **53**, 1410) that in the absence of a catalyst acetoacetic ester can be separated to a considerable extent into its two forms by fractional distillation, and that the enol comes over mainly in the first fractions of the distillate. Thus the enol is the more volatile. In water, the solubility of the enol at 0° is 0·5%, and that of the ketone 11%—more than twenty times as great, whilst in hexane we can calculate from the equilibrium that the enol is ten times as soluble as the ketone. Hence the enol is markedly less polar than the isomeric ketone, and cannot contain a free hydroxyl group: it must be a ring compound (II).

(I.) 

 (II.)

For other keto-enols, although the volatility data are lacking, the same solubility relations can be shown to hold. The effect of the solvent on the relative solubilities of the two forms can be calculated from the proportions at equilibrium; it is not necessary to know the solubilities themselves. The van't Hoff-Dimroth

relation may be put in the form $S_e/S_k = C_e/C_k \div G$, where S_e, S_k are the solubilities of enol and ketone in the solvent used, C_e, C_k their concentrations at equilibrium, and G is a constant for the tautomeric substance, independent of the solvent. It follows that for any given tautomeric substance the ratio of the solubilities is proportional to the ratio of the concentrations at equilibrium. The measurements of K. H. Meyer (*Ber.*, 1912, **45**, 2843; 1914, **47**, 826) have shown that for 11 keto-enols (to which others were added later) including acetoacetic ester, acetylacetone, benzoylacetone, dibenzoylmethane, and acetyl- and benzoyl-camphor, the solubility of the enol relative to that of the ketone is always in the order water <methyl alcohol<ethyl alcohol<benzene< hexane: that is, the enol always behaves as a non-hydroxylic and non-associated substance. We may conclude that the enolic modifications of all these substances are mainly if not wholly in the chelate form.

The ring of 6 atoms with two conjugate double links which occurs in these enols as well as in the ortho-substituted phenols mentioned above, is of enormously wide distribution: it is found in the majority of mordant dyes, in derivatives of alizarin, of *o*-hydroxyacetophenone, of *o*-quinone-oximes, of nitroso-β-naphthol, of the mono- and di-oximes of α-diketones, of hydroxypyrazolones, etc. One reason for this stability may be found by calculating the strain in the ring on the simple principles of Baeyer. Of the six angles in the ring, two are between single valencies, and have the usual value of $2\tan^{-1}\sqrt{2}$, or 109° 28′. The other four are angles between a single and a double link: this is the angle between the line joining the centre of a tetrahedron to one apex and that joining it to the middle point of an opposite edge: the value of this is $180° - \tan^{-1}\sqrt{2}$. Thus the sum of the six angles of the ring in an unstrained condition is $4(180° - \tan^{-1}\sqrt{2}) + 2 \times 2\tan^{-1}\sqrt{2} = 720°$, the exact sum of the angles of a plane hexagon. In other words, this form of ring * is entirely without strain. This conclusion is, of course, subject to the validity of certain simplifying assumptions; but it may be taken to be an approximation to the truth, and to afford an explanation of the remarkable stability of this type of ring.

DYSON PERRINS LABORATORY,
OXFORD.

[*Received, March 19th*, 1925.]

* The same remarks apply to the quinone ring.

NOTES.

Rây's Supposed Triethylene Trisulphide. By George Macdonald Bennett and William Ambler Berry.

More than two years ago one of us made the suggestion (J., 1922, **121**, 2144, footnote) that the substance described by Rây (J., 1920, **117**, 1090) as triethylene trisulphide was probably identical with the well-known diethylene disulphide (1 : 4-dithian). As this suggestion was not accepted (J., 1923, **123**, 2178, footnote), and as further reactions of "triethylene trisulphide" have been described (*J. Indian Chem. Soc.*, 1924, **1**, 63), the question has now been tested by direct experiment. The preparation was repeated as described by Rây, and 1·2 g. of the crystalline substance were obtained, of m. p. 113° (corr.) (Found: C, 39·9; H, 6·5. Calc., C, 40·0; H, 6·7%). The molecular weight of the substance in nitrobenzene solution agrees with the formula $C_4H_8S_2$ (Found: *M*, 128, 126. Calc., *M*, 120).* The substance was compared directly with a specimen of dithian prepared as described by V. Meyer (*Ber.*, 1886, **19**, 3260): this melted at 113°, and its mixture with the supposed triethylene trisulphide melted equally sharply at the same temperature. The two substances had the same characteristic odour, the same remarkable volatility at laboratory temperature, and the same boiling point (200°). Their identity was finally confirmed by examination under the microscope, the crystals being clearly identical both in form and in optical properties.

It is unnecessary to discuss in detail the reactions which have been attributed to this "triethylene trisulphide," but it may be mentioned that among the substances prepared from it the "trisulphone" (J., 1923, **123**, 2174) was evidently identical with Baumann and Walter's disulphone (*Ber.*, 1893, **26**, 1132), and the "disulphone" was presumably an impure specimen of the same substance, and that the case of a nine-membered ring compound yielding a six-membered ring compound under the influence of ethyl iodide in alcoholic solution (J., 1922, **121**, 1279) no longer requires any explanation.

It is evident that in some cases the derivatives described were not homogeneous substances, and this appears all the more probable where they were not purified by recrystallisation. The substance formulated as $(C_2H_4)_3S_3PtCl_4$, for instance (*loc. cit.*, p. 1283), was taken from a succession of crops of material giving analytical figures agreeing approximately with the formula stated. It is

* Sir P. C. Rây is mistaken in supposing that a molecular-weight determination had previously been made by us with the substance; this method of testing the formula was left open to him in the first instance.

now doubtful whether this crop was more homogeneous than those that preceded it.

Our thanks are due to the Department of Scientific and Industrial Research for a grant which has enabled one of us (W. A. B.) to take part in this work.—UNIVERSITY OF SHEFFIELD. [*Received, March 6th*, 1925.]

The Physiological Action of certain Benzothiazoles and Mercaptan Derivatives. By ROBERT FERGUS HUNTER.

4'-AMINO-1-PHENYL-5-METHYLBENZOTHIAZOLE (*J. Soc. Chem. Ind.*, 1923, **42**, 302) and certain related compounds have been found to have a peculiar action on the skin of the face and hands.

Hot solutions of dehydrothiotoluidine in contact with the skin develop an unpleasant form of eczema. The effect is worst between the fingers, and the irritation is intense during the first few days. The skin rises in peculiar, practically colourless blisters, which break, liberating a colourless infectious liquid which spreads the trouble.

Observations of this nature have been made by other investigators with regard to related sulphur compounds. Thus Hofmann (*Ber.*, 1887, **20**, 2251) states that the vapour of *o*-aminophenyl mercaptan has a most detrimental effect on the skin, producing intense irritation and swelling. The author has observed a similar effect produced by the higher homologue of this compound, namely, the thiocresol which results on the alkali fusion of dehydrothiotoluidine.

Bathing the infected skin in hot water relieves the irritation to a certain extent, and treatment with 2% aqueous phenol also has a beneficial action.—THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, S.W. 7. [*Received, February 28th*, 1925.]

Preparation of 1-p-*Sulphophenyl*-3-*methyl*-5-*pyrazolone.* By GEORGE REEVES.

INGOLD (J., 1921, **119**, 329) has put forward evidence in favour of the view that in condensations between tautomeric substances of the keto-enol type and substances which have active hydrogen the tautomeric substance reacts in the enolic form, the unsaturated linking being responsible for the initial condensation and the elimination of water being a subsequent effect. The methods employed to effect condensation between ethyl acetoacetate and phenylhydrazine-*p*-sulphonic acid (Cain, "Manufacture of Intermediate Products for Dyes," 1918 edition, p. 162; Fierz-David, "Grundlegende Operationen der Farbenchemie," 1924 edition, p.

144) do not favour preliminary enolisation of the ester, which is apparently considered to react in the keto-form, and it occurred to the author to attempt the preparation of 1-*p*-sulphophenyl-3-methyl-5-pyrazolone under conditions which would tend to the preliminary enolisation of the ester, this being accomplished by using sodium phenylhydrazine-*p*-sulphonate in somewhat alkaline solution.

A solution of sodium phenylhydrazine-*p*-sulphonate (from 94 g. of the acid) in 750 c.c. of water was made strongly alkaline to litmus and treated quickly at 28° with 65 g. of redistilled ethyl acetoacetate. This dissolved at once and the temperature rose to 36°. After 15 minutes, the solution was heated at 90° for 2 hours, and then acidified with 100 c.c. of hydrochloric acid (28%), a copious precipitate forming rapidly. After 12 hours, the crystalline cake was collected and washed very quickly with a little water. The moist product weighed 226 g. and contained 123 g. of 1-*p*-sulphophenyl-3-methyl-5-pyrazolone (analysis by titration with *N*/10-benzenediazonium chloride). It was very clean and quite pure enough for use as an intermediate for dyes.—The Orchard, Chaddesden, Derby. [*Received, February 11th*, 1925.]

The Micro-estimation of Methoxyl. By John Charles Smith.

In using the method of Pregl (micro-Zeisel) for the estimation of methoxyl, very low results were obtained until it was noticed that the filtrate from the silver iodide gave a further precipitate on dilution with large quantities of alcohol and water. The silver nitrate stock solution had been made by dissolving 20 g. of silver nitrate in 200 g. of 95% alcohol as recommended in the English translation of Pregl's "Die Quantitative Organische Mikroanalyse" (Springer, Berlin, 1923). Reference to the German edition, however, showed that the concentration of the solution should be 20 g. of silver nitrate in 500 g. of 95% alcohol, and this was found to give good results.

The analyses were carried out on a very pure specimen of quinol monomethyl ether, m. p. 56° (OMe, 25·0%).

a. $AgNO_3$ soln., 20 g. in 200 g. of 95% EtOH.			*b*. $AgNO_3$ soln., 20 g. in 500 g. of 95% EtOH.		
Mg. of subs.	Mg. of AgI.	OMe %.	Mg. of subs.	Mg. of AgI.	OMe %.
3·263	5·504	22·3	3·335	6·178	24·5
3·841	4·500	15·5	3·828	7·218	24·9
3·110	4·431	18·8	4·396	8·304	24·9

The University, Manchester. [*Received, March 20th*, 1925.]

Second Report of the International Committee of the International Union of Pure and Applied Chemistry on the Chemical Elements.

INTERNATIONAL ATOMIC WEIGHTS, 1925.

Explanation of the Table.

In this table, the primary standard is, as usual, O = 16·000. We have retained the old value for the secondary standard, Ag = 107·880, although we are of the opinion that this value is slightly higher than the true one. If a more probable value (between 107·870 and 107·876) had been adopted for this secondary standard, many atomic weights dependent upon it (about 42 in number) would be lowered in the same proportion. Since the difference is of slight importance for most purposes, we believe it advisable to avoid the inconvenience of a change until more certain evidence has been obtained. The new table, which is arranged according to the alphabetical order of the International symbols of the elements * (second column), differs in several points from the table published by the former Committee.

First: The third column contains the atomic (or Moseley) numbers of the elements in italics.

Secondly: The atomic weights are given with one uncertain decimal place (except in the case of hydrogen—see below). This is in accord with usual scientific practice. Those persons who prefer fewer decimal places may easily round off the values to suit their needs. For analytical commercial purposes the use of the complete values given in the table is recommended in order to avoid conflicting reports from different analysts.

In accordance with the application of this principle the atomic weights of the following 23 elements have been slightly changed by being expressed with one more decimal place than in the previous table. The values of the fundamental atomic weights given in the table have been used in computing the others.

Ag—Ar—Br—Cl—Cr—Dy—F—Gd—Hg—I—K—Li—Na—Nd—O—P—Pr—Pt—Ra—Rh—S—U—V.

On the other hand, the second decimal has been omitted in the case of krypton; and all decimal places have been omitted in the case of zirconium (for the zirconium material examined up to the present time has undoubtedly been a mixture of two elements), to which the round number 91 is given.

Thirdly: In divers new investigations the atomic weights of 24 elements have been revised. The changes which seem to us

* [In accordance with the usage of the Journal, the elements are given in the table in the alphabetical order of their names.—Editor.]

desirable in the light of the new work are included in the table. The following elements are those affected: Al—B—Be—Ga—Ge—La—Sb—Sc—Si—Sm—Sn—Tl.

A brief summary of the results of these recent investigations is appended so that those who wish to verify the conclusions may easily consult the original records.

Furthermore, since an additional decimal place has been added in the case of most of the fundamental atomic weights, more detailed evidence upon which these changes are bases is cited in conformity with the procedure adopted regarding the other changes made in the old International Table.

Aluminium.—Richards and Krepelka (*J. Amer. Chem. Soc.*, 1920, **42**, 2221) find Al = 26·96 from the ratio $AlBr_3 : 3Ag$.

Recently (in a paper communicated to the *Bohemian Academy* and to the *J. Amer. Chem. Soc.*) Krepelka finds from the ratio $AlCl_3 : 3Ag$, as a mean of 11 very concordant experiments, Al = 26·972, a value slightly higher (by 0·009) than that obtained from the bromide.

Antimony.—Sb = 121·77. Willard and McAlpine (*J. Amer. Chem. Soc.*, 1921, **43**, 797) have determined the ratio $SbBr_3 : 3Ag$ and $SbBr_3 : 3AgBr$.

Beryllium.—Hönigschmid and Birckenbach (*Ber.*, 1922, **55**, 4) find from the ratios $BeCl_2 : 2Ag$ and $BeCl_2 : 2AgCl$ the value Be = 9·018.

Boron.—Baxter and Scott (*Science N. S.*, 1921, **54**, 524) reported the preliminary value B = 10·83. Hönigschmid and Birckenbach (*Anal. Fis. Quim.*, 1922, **20**, 167) find from the ratio $BCl_3 : 3Ag$, B = 10·817—10·838, and from the ratio $BCl_3 : 3AgCl$, B = 10·818—10·842. The authors prefer B = 10·82. Recently Baxter and Scott (*Proc. Amer. Acad.*, 1923, **59**, 21) find from the ratio $BCl_3 : 3Ag$, B = 10·820 as a mean of 22 experiments; from the ratio $BCl_3 : 3AgCl$ (7 experiments), B = 10·824; from the ratio $BBr_3 : 3Ag$ (14 experiments), B = 10·822; from the ratio $BBr_3 : 3AgBr$ (2 experiments), B = 10·812. The mean of all analyses is B = 10·820.

Bismuth.—Hönigschmid and Birckenbach (*Ber.*, 1921, **54**, 1873) find Bi = 209·00 from the ratios $BiCl_3 : 3Ag$ and $BiBr_3 : 3Ag$.

Bromine.—Br = 79·916. Ag : AgBr = 0·574453; AgBr : AgCl = 1·310171. Baxter (*Proc. Amer. Acad.*, 1906, **42**, 202). Br : Ag = 0·740786; Br : AgBr = 0·425547. Hönigschmid and Zinth (*Annalen*, 1923, **433**, 201).

Carbon.—C = 12·000. $CO_2 : C = 2·6660$ (Clarke, "A Recalculation of the Atomic Weights," 4th Ed., *Memoir of the Nat. Acad. Science*, vol. XVI, No. 3).

Chlorine.—Cl = 35·457. AgCl : Ag = 1·32867. Richards and Wells (*Pub. Carn. Inst.*, No. 28, 1905) AgBr : AgCl = 1·310171. Baxter (*Proc. Amer. Acad.*, 1906, **42**, 202).

Chromium.—Baxter, Mueller, and Hines (*J. Amer. Chem. Soc.*, 1909, **31**, 329) $Ag_2CrO_4 : 2Ag$; Baxter and Jesse (*ibid.*, 1909, **31**, 541) $Ag_2Cr_2O_7 : 2Ag$, find Cr = 52·01.

Cobalt.—Co = 58·94. Baxter and Dorcas (*J. Amer. Chem. Soc.*, 1924, **46**, 357) find from the analysis of the chloride that both terrestrial and meteoric cobalt possess the atomic weight 58·94.

Fluorine.—Smith and Van Haagen (*Pub. Carn. Inst.*, No. 267, 1918) find F = 19·00.

Gallium.—Richards with W. M. Craig (*Bull. Soc. chim.*, 1922, **31**, 929) from the ratio $GaCl_3 : 3Ag$ find Ga = 69·716; see also *J. Amer. Chem. Soc.*, 1923, **45**, 1155.

Germanium.—Ge = 72·60. Baxter and Cooper (*Proc. Amer. Acad. Arts and Sciences*, 1924, **59**, 235) find from the ratio $GeCl_4 : 4Ag$ the atomic weight Ge = 72·60. They have confirmed the result by the analysis of the bromide (not yet published).

Holmium.—Ho = 163·4. Holmberg (*Z. anorg. Chem.*, 1911, **71**, 226).

Hydrogen.—The best gravimetric and gasometric determinations give for the atomic weight of this element values lying between 1·0075 and 1·0078. The rounded value 1·008 suffices for all practical purposes.

Iodine.—I = 126·932. Ag : I = 0·849906. Baxter (*J. Amer. Chem. Soc.*, 1910, **32**, 1591).

Lanthanum.—La = 138·90. Baxter, Tani, and Chapin (*J. Amer. Chem. Soc.*, 1921, **43**, 1080) find La = 138·91. Hopkins and Driggs (*ibid.*, 1922, **44**, 1927) find La = 138·89.

Lithium.—Li = 6·940. LiCl : AgCl = 0·29579; LiCl : Ag = 0·39299. Richards and Willard (*Pub. Carn. Inst.*, 1910, No. 25, 1).

Mercury.—Hg = 200·61. Easley, then Baker and Watson (see Clarke's "Recalculation of the Atomic Weights," 4th Ed., 1920, pp. 200—205). Hönigschmid, Birckenbach, and Steinheil (*Ber.*, 1923, **56**, 1212).

Neodymium.—Nd = 144·27. Baxter and Chapin (*J. Amer. Chem. Soc.*, 1911, **33**, 1). Baxter, Whitcomb, and Stewart (*ibid.*, 1916, **38**, 302).

Phosphorus.—P = 31·027. $3AgBr : Ag_3PO_4 = 1·34562$. Baxter and Jones (*Proc. Amer. Acad.*, 1910, **45**, 137); $PBr_3 : 3Ag = 0·836647$; $PBr_3 : 3AgBr = 0·480623$. Baxter, Moore, and Boylston (*ibid.*, 1912, **47**, 585); $PCl_3 : 3AgCl = 0·319509$; $PCl_3 : 3Ag = 0·424507$. Baxter and Moore (*J. Amer. Chem. Soc.*, 1912, **34**, 1644).

Platinum.—Pt = 195·23. Archibald (*Proc. Roy. Soc. Edin.*, 1909, **29**, 721).

Potassium.—K = 39·096. KCl : AgCl = 0·52012; KCl : Ag = 0·69107. Richards and Mueller (*Pub. Carn. Inst.*, 1907, No. 69, 27).

Praseodymium.—Pr = 140·92. BAXTER and STEWART (*J. Amer. Chem. Soc.*, 1915, **37**, 516).

Radium.—Ra = 225·95. HÖNIGSCHMID (*Monatsh.*, 1911, **33**, 253; *Wien. Akad.*, Nov. 1912, 121).

Radon.—Formerly *Niton*. The round number Rn = 222 appears the most probable from radioactive evidence.

Samarium.—Sm = 150·43. STEWART and JAMES (*J. Amer. Chem. Soc.*, 1917, **39**, 2605). OWENS, BALKE, and KREMERS (*ibid.*, 1920, **42**, 515).

Scandium.—Sc = 45·10. HÖNIGSCHMID (*Z. Elektrochem.*, 1919, **25**, 93).

Silicon.—Si = 28·06. BAXTER, WEATHERILL, and SCRIPTURE (*Proc. Amer. Acad.*, 1923, **58**, 245) find from the ratio $SiCl_4 : 4Ag$, Si = 28·063; from $SiBr_4 : 4Ag$, Si = 28·059. Mean of the best series: Si = 28·061.

Sulphur.—S = 32·064. $2AgCl : Ag_2SO_4 = 0{\cdot}91933$. RICHARDS and JONES (*Pub. Carn. Inst.*, 1907, No. 69, 69); $Na_2SO_4 : Na_2CO_3 = 1{\cdot}34016$; $Na_2CO_3 : 2Ag = 0{\cdot}491265$. RICHARDS and HOOVER (*J. Amer. Chem. Soc.*, 1915, **37**, 95).

Thallium.—Tl = 204·39. HÖNIGSCHMID, BIRCKENBACH, and KOTHE (*Sitzungsber. Bayer. Akad. Wiss.*, 1922, 179) find from the ratio TlCl : Ag, Tl = 204·39; and from the ratio TlCl : AgCl, Tl = 204·39.

Thulium.—Tm = 169·4. JAMES and STEWART (*J. Amer. Chem. Soc.*, 1920, **42**, 2022) find Tm = 169·39.

Titanium.—BAXTER and FERTIG (*J. Amer. Chem. Soc.*, 1923, **45**, 1228) find by analysis of the tetrachloride, Ti = 47·85. Since this result is preliminary, no change is recommended.

Yttrium.—Y = 88·9. Mean of the best determinations.

Zinc.—Zn = 65·38. RICHARDS and ROGERS find Zn = 65·376 (*Proc. Amer. Acad.*, 1895, **31**, 158); BAXTER and GROSE find Zn = 65·389 (*J. Amer. Chem. Soc.*, 1916, **38**, 868); BAXTER and HODGES find Zn = 65·381 (*ibid.*, 1921, **43**, 1242).

F. W. ASTON.
GREGORY P. BAXTER.
BOHUSLAV BRAUNER.
A. DEBIERNE.
A. LEDUC.
T. W. RICHARDS.
FREDERICK SODDY.
G. URBAIN.

[Celtium / Hafnium] HÖNIGSCHMID and ZINTL (*Ber.*, 1925, **58**, 453) determined the ratio of the tetrabromide to AgBr with two samples found by THAL JANTZEN (by *X*-ray analysis) to contain (I) 0·57, (II) 0·16% Zr. From I they find the atomic weight of the element to be 178·64 ± 0·09: from II, 178·57 ± 0·03. As the most probable value they give 178·6 ± 0·05.—EDITOR.]

International Table of Atomic Weights of the Chemical Elements.
1925.

	Symbol.	At. No.	At. weight.
Aluminium ...	Al	*13*	26·97
Antimony	Sb	*51*	121·77
Argon	A (Ar)	*18*	39·91
Arsenic	As	*33*	74·96
Barium	Ba	*56*	137·37
Beryllium ..... / Glucinium	Be / Gl	*4*	9·02
Bismuth	Bi	*83*	209·00
Boron	B	*5*	10·82
Bromine	Br	*35*	79·916
Cadmium	Cd	*48*	112·41
Caesium	Cs	*55*	132·81
Calcium	Ca	*20*	40·07
Carbon	C	*6*	12·000
Cerium	Ce	*58*	140·25
Chlorine	Cl	*17*	35·457
Chromium	Cr	*24*	52·01
Cobalt.....	Co	*27*	58·94
Columbium ... / Niobium	Cb / Nb	*41*	93·1
Copper	Cu	*29*	63·57
Dysprosium ...	Dy	*66*	162·52
Erbium	Er	*68*	167·7
Europium	Eu	*63*	152·0
Fluorine	F	*9*	19·00
Gadolinium ...	Gd	*64*	157·26
Gallium	Ga	*31*	69·72
Germanium ...	Ge	*32*	72·60
Gold	Au	*79*	197·2
Helium	He	*2*	4·00
Holmium	Ho	*67*	163·4
Hydrogen	H	*1*	1·008
Indium	In	*49*	114·8
Iodine	I (J)	*53*	126·932
Iridium	Ir	*77*	193·1
Iron	Fe	*26*	55·84
Krypton	Kr	*36*	82·9
Lanthanum ...	La	*57*	138·90
Lead	Pb	*82*	207·20
Lithium	Li	*3*	6·940
Lutecium	Lu	*71*	175·0
Magnesium ...	Mg	*12*	24·32
Manganese ...	Mn	*25*	54·93
Mercury	Hg	*80*	200·61
Molybdenum	Mo	*42*	96·0
Neodymium ...	Nd	*60*	144·27
Neon	Ne	*10*	20·2
Nickel	Ni	*28*	58·69
Nitrogen.....	N	*7*	14·008
Osmium	Os	*76*	190·8
Oxygen	O	*8*	16·000
Palladium	Pd	*46*	106·7
Phosphorus ...	P	*15*	31·027
Platinum	Pt	*78*	195·23
Potassium	K	*19*	39·096
Praseodymium	Pr	*59*	140·92
Radium	Ra	*88*	225·95
Radon	Rn	*86*	222
Rhodium	Rh	*45*	102·91
Rubidium	Rb	*37*	85·44
Ruthenium ...	Ru	*44*	101·7
Samarium	Sm	*62*	150·43
Scandium	Sc	*21*	45·10
Selenium	Se	*34*	79·2
Silicon	Si	*14*	28·06
Silver	Ag	*47*	107·880
Sodium	Na	*11*	22·997
Strontium	Sr	*38*	87·63
Sulphur	S	*16*	32·064
Tantalum	Ta	*73*	181·5
Tellurium	Te	*52*	127·5
Terbium	Tb	*65*	159·2
Thallium	Tl	*81*	204·39
Thorium	Th	*90*	232·15
Thulium	Tm	*69*	169·4
Tin	Sn	*50*	118·70
Titanium	Ti	*22*	48·1
Tungsten ..... / Wolfram.....	W	*76*	184·0
Uranium	U	*92*	238·17
Vanadium	V	*23*	50·96
Xenon	Xe	*54*	130·2
Ytterbium	Yb	*70*	173·6
Yttrium	Y	*39*	88·9
Zinc	Zn	*30*	65·38
Zirconium	Zr	*40*	91

[Celtium / Hafnium] At. number *72*. At. weight 178·6.—EDITOR.]

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 26TH, 1925, AT 4 P.M.

PROFESSOR W. P. WYNNE, D.Sc., F.R.S., the President, occupied the Chair.

The TREASURER made a statement concerning the finances of the Society for 1924, and the Report of Council, together with the Balance Sheets and Statements of Accounts for the year ending 31st December, 1924, was adopted on the proposal of Professor H. E. ARMSTRONG, seconded by Professor G. G. HENDERSON.

REPORT OF COUNCIL, 1924–1925.

I. *Fellowship Statistics.*

THE number of Fellows at 31st December, 1923, was 3978. During the year, 257 Fellows were elected and 8 reinstated, making the gross total 4243. The number of deaths recorded during the period under review was 45; the resignations numbered 121, as against 86 the previous year, while the names of 107 Fellows have been removed for non-payment of annual subscription, and election in the case of 7 new Fellows has been declared void. The number of Fellows at the 31st December, 1924, was, therefore, 3963, and is less by 15 than at the end of 1923.

Among the Fellows whose deaths have been recorded during the year 1924 are Sir James Dobbie, who held the office of President from 1919—1921 and served on the Council for 12 years in all; Professor G. D. Liveing, who was a Vice-President for 7 years and who celebrated in 1923 his 70 years of Fellowship; Sir George Beilby, who was a Vice-President for 3 years and an Ordinary Member of Council for 4 years; and Mr. Otto Hehner, who served on the Council for 4 years. Obituary notices of Sir James Dobbie and Mr. Otto Hehner, prepared by Prof. W. N. Haworth and Dr. B. Dyer, respectively, appeared in the Journal for December.

The congratulations of the Society have been conveyed to Mr. George W. Knox (elected June 16th, 1864) and Mr. Thomas P. Blunt (elected February 2nd, 1865), who have completed 60 years of Fellowship, and to the following, who, during the year, have completed their jubilee as Fellows :

	Elected.
Alfred John Greenaway	April 2nd, 1874.
Frederick William Fletcher	April 16th, 1874.
Harcourt Henry Benjamin Shepherd	May 21st, 1874.
George Christopher	June 18th, 1874.
James Alfred Kendall	Dec. 17th, 1874.
John William Biggart	Feb. 18th, 1875.
Joseph John Acworth	March 4th, 1875.
Joseph Gordon Gordon	March 4th, 1875.

II. *Changes in Officers.*

The Council accepted with much regret in April last the resignation of Prof. Irvine Masson from the office of Secretary on his appointment to a Chair of Chemistry in the University of Durham, and desires to record its appreciation of the ability and zeal with which he conducted the Society's affairs during the two and a half years he filled this position. Dr. T. Slater Price was appointed Secretary until the Annual General Meeting in 1925 to fill the vacancy thus caused.

The Council also accepted with much regret the resignation from the Chairmanship of the Library Committee of Professor J. M. Thomson, whose services in directing the policy of that Committee during a period of twenty years have been invaluable and to whose efforts the comprehensive character of the Library is largely due. Nor should it be forgotten that the Chairmanship, from which he has resigned, is only one of many offices which Professor Thomson has filled to the great advantage of the Society during a period extending over forty-five years. In succession to Professor Thomson Professor J. R. Partington was appointed Chairman of the Library Committee.

III. *Publications.*

The Journal for 1924 contains 2698 pages, of which 2605 pages are occupied by 363 memoirs and 31 notes, the remaining 93 pages being devoted to Obituary Notices, the Hugo Müller and Faraday Lectures, the Report of the General Meeting, and the Presidential Address. The volume of the preceding year contained 400 memoirs and 11 notes, occupying 3258 pages. The activity in British chemical research reflected in the size of the Journal for 1923 was therefore well maintained during 1924. Early in the year, instructions were received from the Council, that, owing to financial stringency, authors should be requested to write their papers as concisely as possible and thus reduce the cost of publication. With this end in view, a new system of refereeing papers was instituted, whereby every paper received by the Society was to be sent to two referees, one of whom must be a member of the Publication Committee. The latter provision necessitated an enlargement of the Committee in order that there should be no delay in the consideration of papers: seven new members were therefore added to that body, increasing its membership to 26. In October the Council deemed it desirable that the Publication Committee should have its own Chairman, and appointed Dr. N. V. Sidgwick to the office.

The transition from the old to the new system involved considerable delay in the publication of papers; this delay was at its

worst in June, when no fewer than 91 papers were in the hands of referees or authors. The congestion was gradually relieved during the succeeding months, and by the end of the year the position was normal, the number of papers under consideration being 20 only.

The appointment of a full-time Editor for the Journal has in the opinion of the Council justified itself, but bearing in mind the possibilities of accident or illness, the work of the Journal cannot be regarded as satisfactorily provided for until he has the assistance of a Sub-editor. How closely he is tied to the work of the Journal will be evident from the fact that to allow him some holiday during last summer, the President undertook to see the August number of the Journal through the press.

The "Abstracts of Chemical Papers" (A. Pure Chemistry) has been issued as a separate publication for which the Bureau of Chemical Abstracts is responsible (*v.* Report of Council, *J.C.S.*, 125, 1924, p. 969). Part I, covering Organic Chemistry and Biochemistry, contained 1396 pages. Part II, covering General and Physical Chemistry, Inorganic Chemistry, Mineralogical Chemistry, and Analytical Chemistry, contained 876 pages.

IV. *Library.*

There is ample evidence of the increasing usefulness of the Library. During 1924 there were 6652 attendances, as against 6403 in 1923, 4486 of these being made by Fellows of the Chemical Society and 2166 by members of contributing Societies; the number of books borrowed was 4509, compared with 4136 the previous year. The additions to the Library comprise 289 books, of which 101 were presented, 560 volumes of periodicals, and 164 pamphlets, the corresponding figures for last year being 343, 494, and 110, respectively. The Library now contains 28,424 volumes, consisting of 8661 books and 19,763 bound volumes of periodicals.

Despite the yearly increase in the number of books and in the number of those who use the Library, the space available for reading has still to be restricted to one room encumbered with stacks of bookshelves, causing inconvenience and discomfort to all concerned. While the urgency of the need for additional accommodation for all purposes, and particularly for the Library, continues to engage the attention of the Council, active steps to meet it seem to be precluded by the present financial stringency.

During 1924, £1769 4*s.* 10*d.* was spent on the Library, and towards this sum £636 15*s.* was contributed by kindred societies. In this connexion, the Council acknowledges its indebtedness to the Institute of Chemistry, which has increased its subscription from

£100 to £250, and to the Research Association of British Rubber and Tyre Manufacturers for a special contribution of £10 10*s*. The Council is also glad to record that the Institute of Brewing now contributes to the expenses of the Library, and desires again to acknowledge that without the substantial help of the contributing societies the advantages afforded by the joint Library scheme could not be adequately maintained.

V. *General.*

The Faraday Lecture entitled " Atomism in Modern Physics " was delivered by Professor R. A. Millikan in the Theatre of the Royal Institution on June 12th, 1924, and the special lecture on " Problems presented by Films on Solid Surfaces " was given by Sir William Hardy on February 26th, 1925, in the Lecture Hall of the Institution of Mechanical Engineers. The continued large attendance at these special lectures, the first series of which was instituted in 1915, affords evidence that their interest and appeal is not exhausted, and, on behalf of the Society, the Council desires to express its great indebtedness to those who deliver them.

The mutual arrangement reached last year between the American Chemical Society, the Society of Chemical Industry, and the Chemical Society, whereby the members of any one of these Societies may obtain the publications of the other two on privileged terms, has been continued.

It has also been arranged to exchange 20 sets of the " Journal of the Chemical Society " from 1915 to 1924 for a like number of sets of the Berichte for the same period. These sets are now obtainable from the Assistant Secretary at £22 each, plus cost of carriage.

The Society was represented by the President at the celebrations of the coming of age of the University of Leeds and jubilee of its parent foundation the Yorkshire College; by Professor F. G. Donnan at the centenary celebrations of the Franklin Institute; by Professor J. C. Philip at the Kelvin centenary celebrations; by Professor T. M. Lowry at the banquet given by the Société Chimique de France; by Professor J. F. Thorpe at the centenary celebrations of the Rensselaer Polytechnic Institute held at Troy, U.S.A. In connexion with the 50th anniversary of the foundation of stereochemistry by van't Hoff and Le Bel, in 1874, the Society was represented by Professor H. E. Armstrong, and by Professor T. M. Lowry at the celebrations held by the Dutch Chemical Society in Amsterdam, and by Sir William Pope at the celebrations organised by the French Chemical Society in Paris.

In response to an invitation from the Royal Institution, the Council appointed Sir William Pope its representative on the

committee formed to organise the celebration of the discovery of benzene by Faraday at the Royal Institution (June 16th, 1825).

Sir William Tilden has been reappointed to represent the Society on the Court of Bristol University; Professor C. S. Gibson, Sir William Pope, and Professor J. F. Thorpe have been appointed to represent the Chemical Society on the Federal Council for 1924; and Professor Lowry was reappointed for a further two years on the Editorial Board of the Journal of Physical Chemistry.

The Congratulations of the Society on the formation of the Indian Chemical Society were conveyed to Sir Prafulla C. Rây, the first President.

The Council has made a contribution of £100 towards the cost of publishing the "Annual Tables of Constants."

The Council has had under consideration the question whether the titles of papers which have been received by the Society should continue to be published in the Proceedings. As in its opinion such publication serves a useful purpose in making known the fact that investigations covered by the titles have reached the stage at which the results of work in progress can be communicated, and as it may avoid overlapping, it has been decided to continue the practice.

The appreciative thanks of the Council have been accorded to General J. B. Dumas for a typescript of the Life of J. B. Dumas, and to Professor P. P. Bedson for a medal of G. Lunge struck in honour of his 70th birthday.

The Harrison Memorial Prize Selection Committee has met during the past year. As reported to the Council, the Committee came to the conclusion that none of the candidates making application complied with the conditions set out in Clause 9 of the Trust Deed and it was again unable to recommend an award of the Prize. Negotiations with the donors of the Harrison Memorial Prize Fund have been initiated with the object of securing, if possible, a modification of the terms of this clause.

The Council desires to record its indebtedness to those Fellows who have contributed to the Annual Reports for 1924.

The present representatives of the Chemical Society on the Bureau of Chemical Abstracts are Professor C. S. Gibson, Professor G. T. Morgan, Professor J. F. Thorpe, and Professor W. P. Wynne. During the past year, as reported to the Council, the Bureau approached the American Chemical Society with regard to the possibility of organising a single publication in the English language of Abstracts of chemical papers; but the correspondence made it clear that opinion on the other side is definitely against such a scheme. In these circumstances the Bureau has devoted itself to developing plans for the unification of British Abstracts; proposals

have been put forward with this end in view and discussed by the Council, which still has the matter under consideration.

VI. *Financial.*

The Finance Committee met on four occasions during the year. Its membership was enlarged from nine to eleven last April, and in May the Treasurer was appointed Chairman of the Committee by the Council.

Last year the Society was faced with an adverse balance of £1628 15*s.* 9*d.*, and, in his report to the Council, the Treasurer pointed out that if the same rate of expenditure were maintained, and no new sources of income were created, the adverse balance for the year 1924 would be between £2000 and £3000. The outlook was serious, because the Society had already been committed to a considerable increase in the amount of editorial salaries consequent on the retirement of Mr. Greenaway, the appointment of a full-time Editor of the Journal, and the establishment of the Bureau of Abstracts.

The Council had, therefore, to consider the best means of reducing the expenditure and increasing the income of the Society, for it was evident that the financial position could only be readjusted by the institution of a period of drastic economy, after which it would be clear how the Society stood as regards the amount of expenditure it could carry with the income available.

After carefully considering various ways and means of securing this object, the Council decided to increase the price to the public of the Journal and Abstracts and of the Annual Reports, to omit printing the List of Fellows for 1924, and to make a charge of 5*s.* 6*d.* to Fellows for the Annual Reports.

The full effect of some of these changes will not be felt until next year, but their influence on the balance sheet of the present annual period has already been considerable. The List of Fellows was not published and this resulted in a saving of £110 4*s.* 9*d.*; further, there were increases in the receipts from the sale of (*a*) the Annual Reports (£250 19*s.* 2*d.*), and (*b*) the Journal and Abstracts (£364 15*s.* 6*d.*).

The Council had also under consideration the question of reducing the large sum of £474 15*s.* 6*d.* which appears in the accounts for 1923 under the item "Authors' Copies," and at an Extraordinary General Meeting on June 26th power was given to the Council to charge authors the cost price of reprints of their papers appearing in the Journal. Before arrangements had been completed to give effect to this change in the Bye-Law, the position had so changed that it was possible for the Council to continue the issue of reprints gratis in a modified form, each author, or part

author, of a paper in the Journal now receiving 10 copies of the paper free of charge. These reprints are supplied without wrappers, but each reprint bears the volume, number, and year of the Journal, and any author can obtain additional copies of his reprints in wrappers by paying the extra cost. The effect of this economy will not be evident until the accounts for the year 1925 are published, but it is estimated that the cost to the Society of authors' copies will be reduced by about one-half.

Nevertheless, in spite of the effect these minor economies would have on the general financial position, it was clear to the Council that they would be insufficient to meet the situation unless the chief expenditure the Society incurs, namely that due to its publications, could be substantially reduced. The chief publications of the Society are the Journal and Abstracts, the cost of which in 1923 represented 65 per cent. of the total expenditure incurred. It was evident that it would be difficult to effect any considerable reduction in the cost of the Abstracts, the volume of which is determined by many conditions over which the Council has no control, and it followed, therefore, that the main burden of retrenchment would have to fall upon the Journal.

Bearing in mind the chief object for which the Society exists, namely, the publication of new knowledge in chemistry, the Council, as announced in last year's Report, decided to strike at the root of the financial trouble and, by creating the Publications Fund, to establish a capital sum the income of which would ultimately be large enough appreciably to relieve the General Funds of the Society from some of the expenses of publication.

In response to the appeal to Fellows issued in January, 1924, the sum of £1434 17*s.* 1*d.* was collected during the year. Some Fellows, who did not wish to subscribe to a capital fund, gave sums to be expended over a period of years, and of these, the sums assigned to the year 1924, together with the income from the capital fund, have provided an amount of no less than £108 10*s.* 8*d.* towards the year's cost of publication. The Council wishes to record its sincere thanks to those Fellows who have contributed so generously, but it is evident that, if the Fund is to be made really effective, it must be substantially increased, and it is with this object in view that the Council has decided to issue an appeal to Manufacturers. All Life Compositions are in future to be added to the Fund, which will also be enlarged by the sum of approximately £4000, payable under the will of the late Sir Alexander Pedler. Nevertheless, until the Publications Fund assumes substantial proportions the need for restriction in the size of the Journal will always exist. Naturally, the need for the most

stringent care fell within the year under review, and it is due, in a high degree, to the loyal co-operation of authors, referees, and the Editor that the exercise of this very necessary economy has been successful; for the saving on the Journal and Abstracts for 1924 is £796 19*s.* 6*d.*

Finally, it will be noticed that the administration expenses are £363 1*s.* less than those of last year despite an increase in salaries and wages of £29 19*s.* 6*d.* This saving is, in a measure, due to a considerable decrease in the item for house expenses and repairs, but it has also been brought about by general economy all round in the administration of the office.

The total savings and additional income for the year from the sources mentioned amount, therefore, to £1994 10*s.* 7*d.*, and the accounts of the Society accordingly show a credit balance of £210 6*s.* 10*d.* despite the fact that there is a fall in the amount of the admission fees for the year of £174 and a decrease of £71 1*s.* 10*d* in the amount received for advertisements.

The deficit incurred in 1923 was met by a sale of 3½ per cent. Conversion Stock to the value of £1500, which Stock was purchased on behalf of the Publications Fund, so that, in effect, the total investments of the Society remain the same as those of last year.

Means of increasing the membership of the Society have been explored. Believing that many candidates desiring to join the Society have been deterred in the past from so doing on account of the initial expense, the Council resolved to remit, for a period, the payment of the admission fee. The effect of this policy, which could not be put into force until towards the end of the year, was apparent in that at the December election 114 new Fellows were elected as against 79 in the previous December. Steps have been taken to bring before Chemists who have not yet joined the Society the advantages of the Fellowship, and it is hoped that the policy of the Council in thus remitting the admission fee will be still further justified in the coming year.

In general, therefore, the financial affairs of the Society for the year 1924 present a very different picture from that of the previous year. It is anticipated that another credit balance will be available at the end of the present year, although it must not be forgotten that the Society will lose some £500 of income owing to the remission of the entrance fees. Fellows will not fail to note that this more satisfactory position has been reached without recourse to that increase in the subscription which was foreshadowed in the Report for 1923.

VII. *Research Fund.*

The applications for grants from the Research Fund received during 1924 number 120, the amount for which application was made being £1802, while the amount granted was £844 15*s*. Owing to the amount applied for exceeding the sum available for distribution, prior consideration has been given to applications received from Fellows. The following grants were made :

	£	*s.*	*d.*
The synthesis of a degradation product of strychnine. J. N. Ashley	10	0	0
Addition reactions of styrene with polar reagents. F. Ashworth	5	0	0
The abnormal influence of the *cyclo*heptane ring on the closure and stability of attached rings. J. W. Baker	10	0	0
(*a*) Preparation of β-arylpropionitriles and derivatives. (*b*) Synthetical investigation of the 3-phenylchromane derivatives. W. Baker	10	0	0
Study of some aliphatic and cyclic sulphides. G. M. Bennett ...	10	0	0
Photochemical researches (continued) : Relation between quanta absorbed and number of molecules reacting. E. J. Bowen	10	0	0
Hydrolytic fission of methoxy-substituted dibenzoylmethanes. W. Bradley	5	0	0
Co-ordination compounds of beryllium and aminobenzoylacetone. H. Burgess	15	0	0
(*a*) Distribution of organic acids between two immiscible solvents (continued). (*b*) Mobility of the fluorine ion (continued). C. R. Bury and C. W. Davies	3	15	0
Investigations on asymmetric synthesis. J. B. Cohen	5	0	0
Bismuthyl compounds of the different saccharic acids. J. B. Cohen	5	0	0
Stereochemistry of *N*-acyl derivatives of amino-acids. W. M. Colles	14	0	0
The reversible addition of amines to azo-compounds. K. Cooper	5	0	0
Polymorphic derivatives of benzil. E. A. Coulson	5	0	0
The application of the Guareschi reaction to quinones. R. Craven	5	0	0
Condensation of dioxytartaric acid with various compounds containing nitrogen. R. H. Dilworth	5	0	0
Isomerism and mobility of dihydromuconic systems. W. M. Duffin	10	0	0
Action of diazo-salts on sulphonamides (continued). P. K. Dutt	2	10	0
Chemistry of the aminotriazole derivatives (continued). P. K. Dutt	2	10	0
Relation between colour and chemical constitution. S. Dutt	15	0	0
Investigations on alkaloids and an attempt to synthesise cryptopine. G. A. Edwards	10	0	0
Influence of the benzoyl group on the mobility of the three-carbon systems. M. D. Farrow	10	0	0
Steric influence of polymethylene rings on the velocity of reaction in which side chains are involved. R. Gane	10	0	0
Reactions of thiophosgene. H. J. George	10	0	0
Solubility influence. S. Glasstone	5	0	0
Determination of physical constants of organo-metallic compounds. A. E. Goddard	5	0	0

	£	s.	d.
Enhanced reactivity of newly formed molecules. F. R. Goss ...	10	0	0
Quasi-aromatic structures. F. R. Goss	10	0	0
Action of halogenating agents on hydroxyanthraquinones (continued). A. Green	5	0	0
Molar complexity of selenium dioxide in alcoholic solution. G. Green	5	0	0
Properties and isomerism of cyclic glutaconic acids. H. Greene	15	0	0
Synthesis of dibromodiethoxythioindigo. Action of acylating agents on substances of an indigoid nature. R. H. Griffith	8	0	0
Attempt to synthesise morphothebaine or its dimethyl ether. J. M. Gulland	8	0	0
Substances derived from methylquinolines (continued). D. Ll. Hammick	15	0	0
Synthesis of amino- and nitro-naphthoic acids. H. A. Harrison	5	0	0
A comparison of the substances obtained by oxidation of *cyclo*-pentadiene with the quinones of the benzene series (continued). A. Hassell	10	0	0
Synthesis of alkaloids and allied compounds. R. D. Haworth	10	0	0
Studies in ring formation. A. T. Healey	10	0	0
Action of the alkali metals on simple and mixed ethers. H. Henstock	10	0	0
Synthesis of chloro-*o*-xylenol (continued). L. E. Hinkel ...	10	0	0
Properties and tautomerism of derivatives of *cyclo*pentadiene (continued). E. L. Holmes	10	0	0
Resolution of antimony compounds of the complex oxalate type. L. H. A. Holmes	5	0	0
Investigation of " Ciba Yellow " and allied substances. E. Hope	10	0	0
Addition of arsenic halide derivatives to unsaturated compounds. A. F. Hunt	5	0	0
Use of aluminium chloride in connexion with the preparation of organic compounds of arsenic. A. F. Hunt	7	0	0
(*a*) Additive reactions. (*b*) Mobility of tautomeric systems. C. K. Ingold	25	0	0
(*a*) Reversibility of additive reactions. (*b*) Tautomerism of dyads. (Mrs.) E. H. Ingold	15	0	0
The thickness of the adsorption layer on a silica surface. D. C. Jones	5	0	0
(*a*) Action of formaldehyde and ammonia on nitromalonic ester. (*b*) Condensation of aluminium ethylate and chloral in carbon disulphide solution. W. I. Jones	5	0	0
Condition of equilibrium between alkali and alkaline earth halides and the alcohols. W. J. Jones	10	0	0
Trivalent carbon compounds. W. J. Jones	10	0	0
(*a*) Condensation products of monobromo-glutaric and -adipic acids with *cyclo*hexanone. (*b*) Preparation of unsaturated monomolecular condensation products of cyanoacetamide with various ketones. W. Kilroy	10	0	0
The solubility products of salts in non-aqueous media. F. E. King	10	0	0
Chromammine salts. H. J. S. King	5	0	0
Optically active sulphonic acids. E. E. Mabbot	5	0	0
Properties and structure of a new oxygenated sesquiterpene aldehyde or ketone. F. H. McDowall	10	0	0

	£	s.	d.
Isomerism of the dinitrobenzidines. G. P. McHugh	5	0	0
Preparation and examination of $\beta\beta$-dipropyl- and $\beta\beta$-dibutyl-acrylic acids, etc. C. J. May	10	0	0
Researches on thallium compounds. R. C. Menzies	10	0	0
New metallic salts and higher aliphatic esters of the simple amino-acids (continued). W. T. J. Morgan	10	0	0
Action of zinc methyliodide on the chloride of glutaconic acid and its derivatives. B. T. Narayanan	10	0	0
Adsorption from solution by various gels in organic solvents. L. E. Outridge	10	0	0
Preparation of certain normal hydrocarbons. S. R. Parsons ...	5	0	0
Tetra-substituted pyrrole derivatives. S. G. P. Plant	10	0	0
The diketone $\alpha : \gamma$-dimethoxyacetoacetic ester. D. D. Pratt ...	10	0	0
Properties of solutions of salts in non-aqueous solvents. H. R. Raikes	5	0	0
Synthesis of trimethylbrazilin. J. N. Ray	5	0	0
Synthesis of oxy-berberine. J. N. Ray	10	0	0
Properties of the cyclic analogues of γ-acetylcrotonic esters. H. L. Richardson	10	0	0
Effect of substituents in the CH_2 group of succinic anhydride and succinyl chloride on the reduction product obtained, and on the course of the scission. E. Roberts	5	0	0
Redetermination of the atomic weight of mercury. P. L. Robinson	10	0	0
Relation between catalytic activity and conductivities of hydrogen chloride in methyl and ethyl alcoholic solutions. S. F. Rogers	5	0	0
The additive reactions of unsaturated cyclic ketones leading to the formation of polycyclic structures. J. Ross	10	0	0
Ring-chain tautomerism. E. Rothstein	10	0	0
(*a*) Dimethoxy phenyl hydrazines and their derivatives. (*b*) Orientation problems in trisubstituted benzene derivatives. L. Rubenstein	5	0	0
Dielectric constants of solutions. J. F. J. Rule	15	0	0
1 : 5-Dicarbonyl compounds. B. D. Shaw...	15	0	0
Attempt to synthesise apofencho-camphoric acid. W. F. Short	15	0	0
Behaviour of urea, thiourea and allied compounds and their derivatives. S. S. G. Sircar	10	0	0
α-Ethyl and $\beta\beta$-dimethyl glutaric acid and its more important derivatives. L. F. Smith	7	0	0
Steric hindrance and alternate latent polarity. R. W. J. Smith	5	0	0
Three-carbon tautomerism. E. A. Speight	8	0	0
Dissociation constants of dibasic acids. C. H. Spiers	10	0	0
Preparation of compounds analogous in constitution to the *iso*-cyanines. H. R. Stevens	10	0	0
Synthesis of dialdehydo-benzoic acids. J. F. S. Stone	5	0	0
Relation between surface tension, density, and chemical composition (continued). S. Sugden	10	0	0
Aliphatic diazo-compounds and the question of their optical activity. T. W. J. Taylor	5	0	0
Heat of wetting of various gels by a series of organic liquids. E. S. Timms	10	0	0
Optical activity of aluminium compounds. E. E. Turner ...	4	0	0

	£	s.	d.
Experiments on the formation of nitrones. C. C. N. Vass ...	10	0	0
Attempt to isolate "sulphur sesqui-oxide" and the compound H_2SO or its salts. I. Vogel	5	0	0
The study of nitrobenzaldehyde hydrazones. A. J. Walker ...	5	0	0
Interaction of bromine with acetic and propionic anhydrides (continued). H. B. Watson	10	0	0
Influence of substituents on the formation of ring structures containing nitrogen. R. W. West	10	0	0
(*a*) Side chain formation in cyclo-paraffins and subsequent synthesis of spiro compounds. (*b*) Constitution of the monochloro- and monobromo-methylsuccinic acids. W. A. Wightman	10	0	0
Temperature coefficient of viscosity of gases. F. A. Williams ...	20	0	0
The effect of the phenyl group on potentially mobile 3-carbon systems. L. T. D. Williams	10	0	0
Total	£844	15	0

A vote of thanks to the Auditors (Professors A. J. ALLMAND, J. S. S. BRAME, and J. F. SPENCER) for their services, proposed by the Treasurer, and seconded by Professor W. E. S. TURNER, was carried unanimously.

Mr. A. CHASTON CHAPMAN proposed a vote of thanks to the Treasurer, Secretaries, Foreign Secretary, Council, and Committees for their services during the year. This was seconded by Professor C. H. DESCH and acknowledged by Professor J. W. MCBAIN.

On the motion of the PRESIDENT, Professors J. F. Spencer, A. J. Allmand, and J. S. S. Brame were elected Auditors for the coming year.

The PRESIDENT then delivered his Address, entitled "Universities as Centres of Chemical Research."

Sir WILLIAM POPE proposed a vote of thanks to the President for his eminent services in the Chair during the past two years and for his Address, requesting him to allow the Address to appear in the Journal. This was seconded by Professor J. C. PHILIP, and carried with acclamation. The PRESIDENT, after acknowledging the thanks of the Society read the report on the election of the Council for 1925—1926:

President.—Arthur W. Crossley.

Dr. CROSSLEY then took the Chair and after expressing to the meeting his sense of the honour conferred upon him continued the reading of the Report.

Vice-Presidents who have filled the office of President.—H. E. Armstrong, W. H. Perkin, Sir William J. Pope, A. Scott, Sir James Walker, W. P. Wynne.

Vice-Presidents who have not filled the office of President.—J. B. Cohen, A. J. Greenaway, G. T. Morgan, James C. Philip, N. V. Sidgwick, J. M. Thomson.

Treasurer.—J. F. Thorpe.

Secretaries.—T. Slater Price, C. S. Gibson.

Foreign Secretary.—F. G. Donnan.

Ordinary Members of Council.—H. Bassett, D. R. Boyd, O. L. Brady, A. E. Dunstan, F. A. Freeth, F. W. Gamble, W. N. Haworth, C. K. Ingold, J. Kenyon, B. Lambert, H. McCombie, G. W. Monier-Williams, T. S. Moore, B. D. Porritt, F. L. Pyman, J. Reilly, G. Stubbs, F. J. Wilson.

RESEARCH FUND.

Income.

	£ s. d.	£ s. d.
To Dividends on :—		
£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock	31 0 0	
£1034 Great Western Railway 2½ per cent. Debenture Stock	20 0 8	
£1142 16s. New South Wales 3 per cent. Debenture Stock	34 5 8	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	33 13 2	
£853 London, Midland and Scottish Railway 4 per cent. Debenture Stock	26 8 10	
£806 Victoria 3 per cent. Stock	18 14 10	
£4498 11s. 0d. 5 per cent. War Loan, 1929/47	224 18 6	
£5827 0s. 9d. 3½ per cent. Conversion Stock	181 0 0	
		570 1 8
,, Income Tax Recovered		76 14 2
,, Repayment of Grants		177 16 1
,, Sale of Apparatus		6 11 3
,, Balance, being Excess of Expenditure over Income, carried to Balance Sheet		45 2 1
		£876 5 3

Expenditure.

	£ s. d.	£ s. d.
By Grants		844 15 0
,, Commission on Recovery of Income Tax		3 16 9
,, Advertisements		4 1 6
,, Cheque Book		1 12 0
,, Longstaff Medal		2 0 0
,, Award to Medallist (Prof. F. G. Donnan)		20 0 0
		£876 5 3

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

	£ s. d.	£ s. d.
To Dividends on :—		
£500 National War Bonds, 5 per cent., 1928	25 0 0	
£500 National War Bonds, 5 per cent., 1929	25 0 0	
£61 15s. 8d. Conversion Stock (6 months only)	2 3 2	
		£52 3 2
By Advertisements (Prize)		1 19 6
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet		50 3 8
		£52 3 2

PUBLICATIONS FUND.

	£ s. d.	£ s. d.
To Transfer from General Account, being Life Composition Fees for year	60 0 0	
,, Subscriptions	115 8 0	
,, Donations	1241 10 5	
,, Interest on Deposit	17 18 8	
		£1434 17 1
By Transfer to General Account—Income applicable to 1924 Publications		108 10 8
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet		1301 10 5
,, Subscriptions in advance		24 16 0
		£1434 17 1

INCOME AND EXPENDITURE ACCOUNT

Income.

	£ s. d.	£ s. d.
To Life Compositions		60 0
,, Admission Fees		528 0 0
,, Annual Subscriptions :—		
Received in advance, on account of 1924	585 0 0	
,, during 1924 ,, ,,	8425 2 0	
,, ,, ,, ,, 1923	469 2 0	
,, ,, ,, ,, 1922 and previous years	31 18 0	
	9511 2 0	
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	600 0 0	
	8911 2 0	
Add Arrears at date : £811 18*s.* ; Estimated to realise as per Balance Sheet	500 0 0	9411 2 0
,, Investments, Dividends on :—		
£787 London, Midland and Scottish Railway 4 per cent. Debenture Stock	24 7 10	
£1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock	35 7 4	
£1400 India 2½ per cent. Stock	35 0 0	
£2400 Bristol Corporation 2½ per cent. Debenture Stock	46 10 0	
£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	84 2 0	
£1200 Leeds Corporation 3 per cent. Stock	27 18 0	
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	45 0 0	
£1200 London and North Eastern Railway 3 per cent. Debenture Stock	27 18 0	
£700 Canada 3½ per cent. Stock, 1930/50	18 19 8	
£2100 5 per cent. War Stock	105 0 0	
£1100 5 per cent. War Bonds	42 12 6	
£600 Funding Loan, 4 per cent., 1960/90	21 6 0	
£13854 8*s.* 3*d.* 3½ per cent. Conversion Stock	430 7 0	
,, Income Tax Recovered	170 15 8	
,, Interest Received—*less* paid	6 12 7	1121 16 7
,, Publication Sales :—		
Journals and Proceedings	2165 4 4	
Abstracts	1614 18 0	
Collective Index, Vols. I–V	133 15 10	
Annual Reports on Progress of Chemistry	634 4 10	
Berichte and Zentralblatt	60 0 0	
	4608 3 0	
Less Publishers' Commission	413 17 10	4194 5 2
,, Proceeds of Advertisements in Journal	623 2 0	
Less Commission	58 13 1	564 8 11
,, Miscellaneous Receipts		56 4 2
,, Donations to Library :—		
Association British Chemical Manufacturers	250 0 0	
Biochemical Society	10 10 0	
Faraday Society	5 5 0	
Institute of Chemistry	250 0 0	
Society of Chemical Industry	100 0 0	
Society of Dyers and Colourists	10 10 0	
Society of Public Analysts	10 10 0	
Research Association of British Rubber and Tyre Manufacturers	10 10 0	647 5 0
,, Subscriptions from other Societies		23 12 6
,, Transfer from Publication Fund		108 10 8
		£16,715 5 0

FOR THE YEAR ENDED 31ST DECEMBER, 1924.

Expenditure.

	£ s. d.	£ s. d.
By Expenses on account of Journal :—		
Editorial Salaries	770 15 1	
Editorial Postages	53 2 8	
Printing of Journal	3244 4 5	
Banding	64 16 1	
Printing of Advertisements	121 8 3	
Addressograph Labels	5 8 7	
Distribution of Journal	427 1 1	
Authors' Copies	448 4 9	
Insurance of Stock	5 5 0	
		5140 5 11
,, Expenses on account of Abstracts :—		
Editorial Salaries	1198 9 9	
Editorial Postages	31 16 9	
Abstractors' Fees	1063 2 0	
Printing of Abstracts	2824 6 4	
Banding	64 16 0	
Addressograph Labels	5 8 2	
Distribution of Abstracts	427 1 2	
Insurance of Stock	5 5 0	
Miscellaneous	40 11 2	
		5660 16 4
,, Lecture Expenses		52 12 10
,, Advance Proofs and Reports of Meetings		84 11 11
,, Annual Reports on the Progress of Chemistry		661 16 5
,, Purchase of Back Numbers of Journal		13 14 5
,, Library Expenses :—		
Salaries	1188 14 3	
Books and Periodicals	453 1 8	
Binding	127 8 11	
		1769 4 10
,, Donations :—		
Annual Tables of Constants	100 0 0	
Journal of Scientific Instruments	50 0 0	
		150 0 0
Administration Expenses :—		
Salary of Staff	1408 10 0	
Wages (Commissionaire, Housekeeper, and Charwomen)	431 17 6	
Coal and Lighting	75 13 7	
House Expenses and Repairs	114 3 11	
Telephone	23 9 9	
Furniture	18 0	
Tea Expenses	41 10 3	
Insurances	20 11 9	
Accountants' Charges	31 10 0	
Commission on Recovery of Income Tax	8 10 9	
Miscellaneous Printing and Stationery	347 3 1	
Postages	192 5 5	
Legal Charges	13 13 0	
Miscellaneous Expenses	91 17 4	
		2801 14 4
,, Transfer to Publications Account		60 0 0
,, Collective Index Vol. VII		110 1 2
,, Excess of Income over Expenditure carried to Balance Sheet		210 6 10
		£16,715 5 0

GENERAL PURPOSES

Liabilities.	£ s. d.	£ s. d.
To Subscriptions received in advance:— at £3 0 0		1086 0 0
,, Sundry Creditors		2026 13 0
,, Bank Account overdrawn		628 12 1
,, Excess of Assets over Liabilities as per last Balance Sheet	25,449 19 7	
Add Excess of Income over Expenditure for Year	210 6 10	25,660 6 5
		£29,401 11 6

Assets.	£ s. d.	£ s. d.
By Investments (value when acquired):—		
£787 London, Midland and Scottish Railway 4 per cent. Debenture Stock	839 3 7	
£1520 14s. 3d. Cardiff Corporation 3 per cent. Stock	1650 0 0	
£1400 India 2½ per cent Stock	1316 1 0	
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070 2 0	
£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	3572 0 4	
£1200 Leeds Corporation 3 per cent. Stock	1143 1 0	
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923-53	1460 13 6	
£1200 London and North Eastern Railway 3 per cent. Debenture Stock	1033 11 0	
£700 Canada 3½ per cent. Stock, 1930/50	704 8 6	
£2100 5 per cent. War Stock, 1929/47	1995 0 0	
£1100 5 per cent. National War Bonds, 1929/47 ...	1045 0 2	
£600 4 per cent. Funding Loan, 1960/90	480 0 0	
£11,873 3½ per cent. Conversion Stock	8987 2 2	
(Market Value £22,584 10s. 4d.)		26,296 3 3
,, Sundry Debtors		2518 11 0
,, Subscriptions in Arrear £811 18s. Estimated to realise		500 0 0
,, Insurance paid in advance...		68 11 6
,, Cash in Hand		18 5 9
		£29,401 11 6

RESEARCH FUND

	£ s. d.	£ s. d.
To Excess of Assets over Liabilities as per last Balance Sheet	14,507 6 3	
Less Excess of Expenditure over Income for Year	45 2 1	14,462 4 2
		£14,462 4 2

	£ s. d.	£ s. d.
By Investments (value when acquired):		
£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock	1010 0 0	
£1034 Great Western Railway 2½ per cent. Debentures	1049 15 11	
£1142 16s. 0d. New South Wales 3 per cent. Stock	1000 0 0	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002 16 9	
£853 London, Midland and Scottish Railway 4 per cent. Debenture Stock	1009 18 9	
£806 Victoria 3 per cent. Stock, 1929/49	706 6 2	
£4498 11s. 0d. 5 per cent. War Stock, 1929/47	4267 4 10	
£5827 0s. 9d. 3½ per cent. Conversion Stock	4398 14 10	
(Market Value £13,514 6s. 9d.)		14,444 17 3
,, Cash at Bank		17 6 11
		£14,462 4 2

		£14,462	4	2		£14,462	4	2

THE EDWARD FRANK HARRISON MEMORIAL TRUST

To Excess of Assets over Liabilities as per last Balance Sheet		1201	3	0	By Investments (value when acquired):—			
Add Excess of Income over Expenditure for Year		50	3	8	£500 National War Bonds 5 per cent. 1928	500	0	0
					£500 National War Bonds 5 per cent. 1929	500	0	0
					£61 15*s.* 8*d.* 3½ per cent. Conversion Stock (Market Value £1106 3*s.* 0*d.*)	50	1	5
							1050	1	5
					Cash at Bank		201	5	3
		£1251	6	8			£1251	6	8

PUBLICATIONS FUND

To Subscriptions received in advance			24	16	0	By Investment £1981 8*s.* 3*d.* 3½ per cent. Conversion Loan (Market Value £1560 7*s.* 0*d.*)		1500	0	0
,, Excess of Assets over Liabilities as per last Balance Sheet	235	2	7			,, Cash at Bank on Current Account	61	9	0	
Add Excess of Income over Expenditure for Year	1301	10	5					61	9	0
				1536	13	0				
				£1561	9	0		£1561	9	0

I have examined the above Balance Sheets and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant.

23 QUEEN VICTORIA STREET, E.C. 4
February 11th, 1925.

Approved { J. F. SPENCER, A. J. ALLMAND, J. S. S. BRAME.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 26th, 1925.

By WILLIAM PALMER WYNNE, D.Sc., F.R.S.

Universities as Centres of Chemical Research.

FOR this, my valedictory address, I have chosen as my text part of a sentence occurring in the review of the position and prospects of chemical research in this country with which my distinguished predecessor, Professor Meldola, closed his period of office in 1907—seven years before the outbreak of War. His choice of subject was singularly appropriate in view of the fact that, in the preceding year, the Jubilee of the foundation of the coal-tar colour industry by Perkin had been celebrated at an international gathering in London, and the occasion seized to emphasise the striking object lesson thereby furnished of the application of scientific research to industrial purposes.

Now, in this seventh year after the Armistice, the centenary of an equally important event—that of Faraday's discovery of benzene—is to be celebrated. Rightly and naturally, the Royal Institution which was the birthplace of this puzzling yet fascinating hydrocarbon, has assumed responsibility for ensuring due recognition of its historic discovery. While we as chemists yield place to no one in our recognition of the outstanding importance of the isolation of benzene, none of us will wish to forestall those who assemble in the historic lecture theatre in Grafton Street on Tuesday, June 16th, to do homage to Faraday's merit as an investigator and we can safely leave them to utilise the opportunity of illustrating afresh the significance of pure chemical research in the progress and development of chemical industry.

The creation, discussion and publication of new knowledge in chemistry being the objects for which this Society was founded and exists, the position and prospects of chemical research in this country can never be without interest to its Fellows. Therefore, at a period removed by almost as many years from the end of the War as the date of Professor Meldola's address preceded its outbreak, it seems worth while not so much to endorse his indictment of the conditions which hampered the prosecution of research early in the century and are not without adverse influences to-day, as to consider how far, if at all, the outlook for chemical research has improved during this interval. I admit the difficulty confronting anyone like myself who, with a more restricted vision, attempts

to follow a man so eminent in his profession and so well equipped as Professor Meldola was to pronounce judgment on an issue of this kind. Nevertheless I do venture to think that were he living now, he would be among the first to recognise that the War in changing the face of the world has incidentally altered the estimation in which chemistry is held in this country.

Sir James Dobbie, whose recent death we so much lament, and Sir William Pope have dealt in their addresses from this Chair with the War effort of British Chemistry and shown how true in fact was Meldola's appreciation of its eminence expressed in the words "It is impossible to survey the achievements of our little army of workers . . . . without coming to the conclusion that neither in zeal or originality nor in any of the qualifications which have enabled other nations to advance the cause of chemical science, are we lacking in this country."

This tribute, which the War more than justified, was followed by a discussion of the question whether " the output of work . . . . is really representative of the productive capacity of the nation " leading first to the definite conclusion that " this is far from being the case " and secondly to an analysis of the causes contributing to so unfortunate a result. Attention was then directed to " the character of the institutions in which research is being or might be expected to be carried on " and, after giving credit to establishments endowed or maintained for the conduct of research, Meldola directed his inquiry to the Universities, University Colleges and Institutions of University rank and to the numerous Polytechnics and Technical Schools founded to promote technical education under the Acts of 1889 and 1890.

Quoting again from the address, the opinion is expressed that a few of these institutions of University type " such, for example, as the Victoria University at Manchester, where a recognised school of Chemistry has been created, and Cambridge, whence contributions of importance reach us from time to time, are doing good service in the cause of chemical research." They, however, are regarded as the exceptions, whereas, judged by the Continental standard, " many of our Universities are distinct failures as centres of chemical research and the total output of work from University laboratories is by no means worthy of the great traditions of this country as a pioneering nation in scientific discovery." That the failure of the Technical Schools to advance chemical science should lead to a feeling of profound disappointment need cause no surprise in view of Meldola's long connexion with the pioneering work of the City and Guilds of London Institute.

In discussing the reasons for this failure on the part of educational

institutions to avoid what he calls "the enormous submergence of research talent" going on in the United Kingdom, Meldola indicates as contributing to it first, the relatively few openings in industry; secondly, the inadequate salaries paid to assistants and demonstrators; and thirdly, the inability of promising students to remain after graduation, owing to imperative necessity compelling them to proceed at once from the college to some breadwinning occupation. As counteracting agencies he regards one of the most valuable to be the system of awarding "scholarships to men of approved ability to enable them to carry on original work after finishing their college training" and refers specifically to the Scholarships given by the Royal Commissioners of the 1851 Exhibition, by the Salters' Company and by the Carnegie Trust for the Universities of Scotland.

With your permission, I propose to examine these conclusions—not in any spirit of criticism but with the sole object of considering how far they apply to post-War conditions and what additional remedies, if any, can be suggested to check, if not prevent, the wastage of the research faculty.

Output of Research from Universities and Technical Colleges.

In the first place some estimate must be formed of the output of research from Universities and kindred institutions on the one hand and from Technical Colleges on the other. If based, as seems inevitable, on the number of chemical papers published from their laboratories, the list must include purely theoretical discussions, which may vary in importance, as well as contributions dealing with new experimental work. Moreover, the discrimination of papers which seem to be purely physical, physiological or metallurgical in outlook is not free from difficulty unless regard is had to the Department to which the contributor is attached. With these considerations in mind, the following table has been compiled as the result of a scrutiny of the papers published in the journals indicated:

Summary of Chemical Papers published from Universities and Colleges of the United Kingdom during the three six-year periods: 1901—06; 1908—13; 1919—24.

	Trans.* Chem. Soc.	Proc. Roy. Soc.	Faraday Soc. Trans.	J. Soc. Chem. Ind.	J. Amer. Chem. Soc.	Total.
1901—06	747	107	—	11	0	865
1908—13	1132	75	38	25	1	1271
1919—24	1268	56	45	70	25	1464

* The total number of papers contributed to the Transactions from all other sources during these six-year periods was 226, 359 and 406 respectively.

Distribution of these Papers.

	1901—06.	1908—13.	1919—24.
Oxford University	18	89	140
Cambridge University	82	122	142
Manchester University	91	139	84
Imperial College (R.C.S. and C.T.C.)	101	114	143
Percentages	33·8	36·5	34·8
London University Colleges and Medical Schools (13) *	161	244	206
Modern English Universities and University Colleges (11) †	197	252	375
Welsh University Colleges (3)	28	42	47
Scottish Universities (4)	68	85	154
Irish Universities and Colleges (6)	46	53	40
Percentages	57·8	53·2	56·1
Polytechnics and Technical Colleges (20)	73	131	133
Percentages	8·4	10·3	9·1

* Excluding Imperial College.
† Excluding Manchester University.

Of the deductions that can be drawn from these figures there is one which we, as chemists, cannot but regret, remembering the conspicuous part played by Sir Henry Roscoe, first in promoting two Bills for assisting technical education which failed to reach the Statute Book and, afterwards, in aiding the passage through the Commons of the Technical Education Acts to which reference has already been made. If, as seems to be the case, there are some 180 Technical Schools in the United Kingdom,* financed under the provisions of those Acts and equipped with Chemical Departments, and 90 per cent. of them have failed to contribute a single original paper to any of the journals quoted during the period under review or previously, it is evident that their failure to prosecute chemical research has become stereotyped. When it is remembered that the staffs of these schools include chemists who before appointment had shown themselves imbued with the research spirit and, given the opportunity, would doubtless have diffused it among their colleagues, this sterility must be attributed not to them but to the conditions under which their work is done. The conclusion to my mind is inevitable that in the opinion of the great majority of the governing bodies of these Institutions the terms "technical education" and "trade school training" are synonymous at least so far as chemistry, pure or applied, is concerned.

It is the University contribution, however, with which this address is chiefly concerned. Inspection of the table will show

* Cf. "Official Chemical Appointments, 1924," pp. 86—113, issued by the Institute of Chemistry.

that the year 1914, which was more prolific than 1913, has been omitted together with the four War years, but 1919, almost, if not quite, the worst, is included in the last six-year period. Its inclusion may serve to balance the abnormal research activities of the later years, particularly in view of the fact that the peak in the graph of the number of papers plotted against years seems already to have been passed. Taking the figures as they stand, it is evident that in measuring the effort of the other Institutions in terms of the productivity of Manchester and Cambridge, Meldola underestimated the research output of the United Kingdom in the years preceding 1907. On the other hand, it is clear that the improvement which he descried in comparing successive decades has increased by 47 per cent. and 69 per cent. when the two later periods tabulated are compared with the first.

The approximation to uniformity with which each of the three groups in the table has maintained its position, notwithstanding these increases in the total number of papers published, is accidental, but in three cases only, and these in the difficult post-War period, is there any departure from the steady rise in productivity. The apparent uniformity, however, is not without interest, even if unexpected, and may be construed to mean that the Chemistry staffs of these Institutions, including those shown in the last line, realise fully the value and importance of research as an adjunct to teaching and within the means at their disposal cultivate it assiduously.

Causes restricting the Output of Research in Universities.

I turn now to consider the question whether these means are adequate or whether in Meldola's words there is not still "much work ahead of us before the environment in which our workers find themselves is properly cleared from obstruction." The modern Universities have in nearly every case sprung from University Colleges and these in a more remote past from Colleges to which the Founder's name more often than not was attached. These Institutions in their early days experienced many difficulties, of which the endurance of poverty was by no means the least. Readers of Sir William Ramsay's life will remember how many of them were barely saved from extinction by the opportune grant of a subsidy from the Government which in course of time has grown to be £1,500,000 and is shared in now by Oxford and Cambridge. One result of that early penurious existence was the inevitable tendency on the part of the administrative bodies to judge the success or the need of a department by the number of students working in it and another, the disposition to regard all departments

as of equal value or importance. If to both of these impediments be added the relatively high maintenance cost of laboratory provision and upkeep, it will be no matter for surprise to the historian of the last 50 years that the long and arduous struggle to surmount these traditions is not yet over.

How welcome it would be, for a change, if financial circumstances rendered it possible for inquiries to be more often directed towards the number of postgraduates engaged in research or made with reference to the number of hours per week during which each member of the staff is able to pursue research. Teaching, in the sense of training students for a degree, is not the only function of a University—the Statutes of the newer Universities leave us in no doubt on the point even if assurance be needed. Beyond such teaching, all important as it is, lies the training of the postgraduate which will always be the more difficult of the two if conducted, as it surely ought to be, in the spirit so admirably portrayed by Principal Sir James Irvine in the following extract from his address to the Chemical Section of the British Association meeting at Hull:

"There are few more harassing duties than those which involve 'the direction of young research chemists. . . . I am well aware 'that scorn has been poured on the idea that research requires 'training. . . . Individual attention is the first necessity and the 'educative value of early researches is largely derived from the 'daily consultations at the laboratory bench or in the library. Many 'research supervisors find it difficult to enter sympathetically into 'the mental position of the beginner, yet if the pupil is to derive any 'real benefit from his difficulties, his adviser must for the moment 'place himself in the position of one equally puzzled, and must lead 'his collaborator to sum up the evidence, and arrive at the correct 'conclusion for himself. The policy thus outlined is, I believe, 'sound but it makes severe demands on patience, sympathy and, 'above all, time. Research supervision, if conscientiously given, 'involves the complete absorption of the director's energy and 'leisure."

The Arts Faculty is the most numerous and usually the best organised in our modern Universities. Its members have no personal experience of laboratory teaching, inseparable from curricula in science subjects, pure and applied including medicine, and can devote to their own intellectual pursuits the hours which in our Departments it consumes. Were equality of treatment afforded to both sides of University life, the limitation of teaching duties to part only of the working day rightly conceded to our Arts colleagues would, if accorded to laboratory subjects, give to the research side

of our work not odd hours or half days but the equivalent of all the afternoons. Until this becomes the normal feature in laboratory subjects, with the corollary of increased staffs to make it possible, we must not slacken in our educative effort to secure such recognition for our work.

Who does not know and sympathise with the dilemma with which the younger members, shall we say, of the staff of a Chemistry Department are confronted, well knowing that the avenue to promotion is research and yet reasonable opportunities for its pursuit cannot be provided, owing to the financial embarrassments by which University efficiency is retarded? Is the training of undergraduates to suffer, so that research may be kept going, or is the zeal for research to wane until the 'thirties come when its spirit, once damped, is difficult to rekindle? It is this "submergence of research talent" within the Universities themselves which needs first to be remedied.

Whether, under post-War conditions—when the call for economy becomes more, not less insistent—such an increase in Staffs as would be required to equip adequately the research laboratories of our Universities can be provided is more than doubtful, but none of us can regard the present position with any degree of satisfaction. Those who make the quinquennial visitation of Institutions of University rank in connexion with the allocation of State aid are perhaps less accessible to representations from heads of Departments than before the War, but they cannot be in any doubt about the magnitude of the problem with which University education may soon be confronted. It is nothing less than this—can each of the modern Universities, without reference to its neighbours, continue to teach all subjects to the same level and yet remain efficient as contrasted with Continental or American Institutions? The question might still be asked even if they were adequately endowed, which they are not. In the present straitened circumstances, is there any more prudent course than for each to strive for the utmost possible development of a restricted number of subjects in pure or applied science and to be content with a less complete provision for the remainder? In the fierce competition of the modern world—to aid our country in facing which is not one of the least important functions of University training—as in War, nothing lower than the best is of any avail. The problem is: Are we in a position to meet the ever-increasing demand for more intensive study and research in the domain of pure and applied science without either ample endowment, of which there is no prospect, or a radical change of policy in which the good of the community must overrule individual susceptibilities and local pride?

Postgraduate Research Scholarships.

I have dealt with some of the difficulties which handicap the research output of University staffs. Without research students, the handicap would be largely prohibitive. Apart from those in whom the desire to become investigators is inborn, research students are attracted either by the prize of a higher degree or by the prospect of finding employment which experience of research may afford. Without the provision of Scholarships, these opportunities are denied to graduates whose parents cannot afford the cost of maintenance during an additional period of non-remunerative work. Yet experience shows that in many cases it is this type of student which, given the opportunity, makes the most of it, benefiting alike his country and himself. As the position with regard to the provision of research scholarships has undergone important changes within the last ten years, a brief summary of the conditions attached to, and the results achieved by, the three Scholarship schemes mentioned by Meldola may not be out of place.

The 1851 *Exhibition Scholarships.*—First in point of time was the generous scheme of scholarships, and later of bursaries, established by the Royal Commissioners of the 1851 Exhibition. Inaugurated in 1891, this effort represented only one aspect of the Commissioners' promotion of Science, Art and Industry. It continued in operation, so far as Science Scholarships were concerned, until 1915, was resumed in 1919 and placed on a new basis in 1922. Under the scheme, each modern University in the United Kingdom, together with certain University Colleges and Dominion Universities, was invited to nominate a candidate for a scholarship of £150 * a year, tenable for two years and renewable in approved cases for a third. If the Commissioners were satisfied that the graduate nominated had given "distinct evidence of capacity for research" the scholarship was awarded to enable him "to continue the prosecution of science with the view of aiding its advance or its application to the industries of the country." To it was attached one most important condition: the Scholar was "required, in absence of special circumstances, to proceed to an Institution [at home or abroad] other than that by which he was nominated." In 1900, bursaries of £70 † tenable for one year were founded to enable graduates in science with honours to obtain a year's training in research so as to qualify for a scholarship. Through the kindness of the Secretary to the Commissioners, I have had access to the records for the years 1891 to 1921, from which the following tables have been compiled:

* Raised in 1919 to £200 and in 1921 to £250.

† Increased in 1919 to £100.

(i) Distribution of 1851 Exhibition Scholarships among Modern Universities, University Colleges and Dominion Universities.

	English.	Welsh.	Scottish.	Irish.	Dominions.	Total.
1891—1914 (24 years)	197	22	62	36	99	416
1919—1921 (3 years)	18	6	5	6	20	55
	215	28	67	42	119	471

(ii) 1851 Exhibition Scholarships awarded in Chemistry, 1891—1914.

	Total number awarded.	Number awarded in Chemistry.	German doctorates in Chemistry gained by Scholars.
United Kingdom	317	157	77
Overseas Dominions	99	30	18

From these data, it is obvious that practically one half of the Scholars were chemists, all of them migrants from the Universities which trained them and many adding to the stimulating experience of a new environment the knowledge of another people and another language. It has been an interesting study to note how many of our University staffs have been recruited from among these scholars. Recalling the figures shown in the first table, it can be no mere coincidence that the increased output of research synchronises with the development of this scholarship scheme—rather, the two are related as effect and cause. The same view, probably, would be endorsed in respect of research in each of the subjects other than Chemistry aided in like manner by the Commissioners of the 1851 Exhibition.

Since the War, owing partly it may be to the alteration in the value of money and partly to the operation of another scheme of more recent date for the training of research students, these scholarships have been replaced since 1921 by a smaller number, carrying a grant of £300, designed to enable the investigator with three or four years' research experience to his credit to continue working for an additional period without the distraction of teaching or other form of employment. Scholarships of this type, such as the Beit Fellowships or those associated with Sir William Ramsay's name, have become more frequent since the War, and already have justified their inception as aids to research.

The Carnegie Scholarships.—Whereas the Research Scholarships of the 1851 Exhibition have been open to all Universities, those awarded under the Carnegie Trust established in 1901 are limited to Scottish graduates nominated by Professors or Lecturers in Scottish Universities. The scheme comprised scholarships of the value of £100 * tenable for one year but renewable, if deemed

* Now £75.

expedient, for a second year, and Fellowships of the value of £150 * tenable for two years. Unlike the awards of the 1851 Exhibition these scholarships and fellowships can be and for the most part are held in the University in which the holder has graduated. The facts set out in the following table have been collated from the Official Record of the work of the Trust during the first two decades of its operation 1903—1923, published last year, with a copy of which I have been furnished by the kindness of the Secretary of the Trust:

Distribution of Carnegie Scholarships and Fellowships.

Total number of individuals elected to Scholarships and Fellowships (1903—1923)		375
Total number of Scholars and Fellows in Chemistry		105
The number of these Scholars who did not proceed to Fellowships was		72
The number of these Fellows appointed, 20 of whom had previously held Scholarships, was		33
The number of individual Scholars and Fellows who published research work was		72
The number of papers published by them was		
(*a*) In one name	65 (16 abroad)	
(*b*) In two or more names	137 (8 abroad)	

No words of mine are needed to emphasise the value and importance of the work of the Carnegie Trust; all branches of learning are fertilised by its aid, but Chemistry as would be expected receives the largest amount of assistance.

The Salters' Company's Fellowships.—Although necessarily conceived on a much smaller scale than either of the preceding schemes, the fine effort of the Worshipful Company of Salters has been no less successful in promoting research. The earlier scheme, initiated in 1894, provided three Research Fellowships in Chemistry, two of the value of £150 each, of which one was attached to the City and Guilds Central Technical College, and the third of £100. Having served its purpose, it was replaced in 1918 by the foundation of the Salters' Institute of Industrial Chemistry, designed, among its objects, to enable post-graduates with some experience of research to undergo further training for a career in Industrial Chemistry, the Fellowships awarded to this end being normally of the value of £250—£300.†

Establishment of the Department of Scientific and Industrial Research.

During the War, as already indicated, the 1851 Exhibition scheme fell into abeyance and now has been based on an entirely

* Now £250.

† It may be of interest to record the fact that Dr. M. O. Forster, whose services to the Society as Secretary and as Treasurer are gratefully remembered, was in 1894 the first Salters' Fellow at the Central Technical College, and in 1918 the first Director of the Salters' Institute.

different footing, but, most fortunately, there was founded in 1915 an organisation the activities of which are well defined by its title—I refer to the Department of Scientific and Industrial Research. In creating the opinion which led to the establishment of the Department, Fellows of this Society may claim to have had their part. In 1915, Sir William Crookes was President of the Royal Society and under his Chairmanship a meeting of chemists was held in that Society's rooms on February 2nd, followed by two meetings, with Professor Meldola in the Chair, on February 15th and March 10th, at which the serious position facing the chemical industry was discussed, a memorial to the Government prepared and an interview sought with the Prime Minister. At the interview on May 6th, 1915, the Ministers present being Mr. Runciman, President of the Board of Trade, and Mr. Pease (now Lord Gainford), President of the Board of Education, some 20 chemists, grouped as representatives * of our own Society (including its President, Dr. Scott, and the officers), and of the Royal Society, introduced by Sir William Crookes, advocated not only the formation of a Central National Advisory Committee, composed mainly of chemists and chemical manufacturers, to recapture the lost chemical industries but also the importance of research in connexion with any such effort. After speeches in support of the memorials submitted, Mr. Pease announced that the Government had consented to the preparation of a scheme for aiding research work, and on July 23rd, 1915, Mr. Arthur Henderson, who had succeeded him as President of the Board of Education, issued the " Scheme for the organisation and development of scientific and industrial research " as a white paper. In this historic document the opening statement runs :

" There is a strong consensus of opinion among persons engaged 'both in science and industry that a special need exists at the 'present time for new machinery and for additional State assistance 'in order to promote and organise scientific research with a view 'especially to its application to trade and industry."

Eighteen months later, on Friday, December 1st, 1916, Lord Crewe announced to a deputation consisting of some 150 representatives of science pure and applied, meeting in the hall of the Institution of Civil Engineers, that the work of the Committee of the Privy Council for Scientific and Industrial Research and that of its Advisory Council (of which Professor Meldola himself was an original member), associated from its inception with the

* Including a Vice-President of the Institute of Chemistry (in Professor Meldola's absence through illness), the President of the Society of Chemical Industry and the President of the Society of Public Analysts.

Board of Education, had been established as a separate Government Department. From that time onward, provision for scientific and industrial research has been recognised as a duty incumbent on the State. Although, as is the habit of our countrymen, there has been criticism of the work of the Department, I think all who are in a position to pass a considered judgment will concur in the view that, whether it be in the promotion of research associations to aid industry, or in the provision of maintenance grants for the training of graduates in research methods, or in the support of national institutions transferred to its care, the D.S.I.R. has done a service to science and the country so great as to be almost incredible in the light of pre-War neglect.

If attention be confined to the grants made for research training in those branches which have industrial applications, it will be found that the annual expenditure from 1920 onwards has been between £40,000 and £50,000; the table shows, in part, the results achieved which are embodied in the annual reports of the Department to Parliament:

	Total number of grants.	Grants for chemical research made to		Number of published papers recorded by the Department in	
		graduate students.	independent workers and Research Assistants.	all subjects.	Chemistry.
1919—20	109	29	22	40	13
1920—21	202	95	20	122	65
1921—22	260	135	20	143	78
1922—23	290	145	11	126	80
1923—24	279	141	14	152	88

The D.S.I.R. warns us that the provision of maintenance allowances for training in research must not be regarded as a permanent feature of its activities, but it may well be hoped that the date of this withdrawal lies in the remote future, unless provision is made by the State for Universities themselves to bear the cost. It is unquestionably the case that to the provision of these grants is due the rapid revival of research schools after the War, nor can we lose sight of the fact that those students to whom a renewal of the grant for a second year has been made have thereby been enabled to qualify by residence for the Ph.D. degree.

Institution of the Research Degree of Doctor of Philosophy.

The institution of the Ph.D. degree was itself a War measure. In view of the likelihood that German Universities would not be frequented by students from the Allied or Associated countries until after the lapse of an interval of years from the making of

Peace, inquiries were set on foot towards the end of 1916 through the Foreign Office and the Board of Education to ascertain whether British Universities could make provision for research students from America or the Overseas Dominions who, normally, would have studied in Germany. Such provision, it was recognised, would involve the institution of a research degree corresponding with the German Doctorate of Philosophy. As the outcome of conferences and discussions, these Universities in May, 1917, agreed in principle with the view that postgraduate research leading up to a degree should be organised for home or overseas students. A year later they approved the draft ordinances for the new research degree of Ph.D. It is not wholly without interest to recall the pleasure with which their representatives on the previous day had received from Mr. Balfour (now Lord Balfour) at the Foreign Office an assurance of his satisfaction at the steps contemplated " to make attendance at our Institutions more attractive to students from the United States, France, Italy and other Allied countries." Those steps, need it be said, would have involved the expenditure of large public funds if our modern Universities were to be put in a position to furnish the equipment and offer the amenities to which American and Overseas students are accustomed. Any hope that such steps would be taken foundered—like many another hope of that time—in the economic storm which followed at no long interval in the wake of the War.

This failure to provide travelling scholarships brought about a difference in status between home and overseas candidates which ought not to be overlooked—those at home are not required to leave the University in which they have graduated while carrying out research for the doctorate. We, in Sheffield, at the first of the conferences just mentioned, urged that the research work of all candidates for the Ph.D. degree should be conducted in a second University, as was necessarily the case with those 1851 Exhibition Scholars who obtained the German doctorate. The proposal received little or no support and has not been revived. One objection, widely entertained, was to the effect that such a condition would operate harshly in the case of otherwise excellent students who, in the absence of adequate postgraduate scholarships, could not find the means to enable them to live away from home during the minimum period of two years' research training required for the degree.

Yet, from the student's point of view, who can doubt the great advantage accruing from the opportunity of working in a different environment during the last years of his training? Other things being equal, which of the alternatives will give the research student

the more valuable experience—to stay in the laboratories in which he has pursued his Honours course, or to have a complete change in surroundings? In the one case, the attitude of teacher to student and *vice versa* is unlikely to suffer much change, but in the other—there being no link with the immediate past—supervisor and postgraduate can begin their co-operation from an entirely different standpoint. Beyond all question, what is needed among research students and those promoted therefrom to junior staff appointments is a wider experience than can be gained by living in the atmosphere of one laboratory, associated with the same teachers and fellow students, during five or six years. In interviewing candidates for higher posts there is nothing arouses more regret than this want of experience—from which before the War the Commissioners of the 1851 Exhibition provided some way of escape.

As there is no immediate prospect that any step can or will be taken by British Universities to meet this defect—as surely it is—in the regulations for the Ph.D. degree, the question is worth asking: Cannot a solution of the difficulty be found in another way? Under Mr. Fisher's guidance, the Board of Education instituted a series of State scholarships, planned on novel lines, to Universities, thereby adding to the large number of entrance scholarships already in existence. Until the D.S.I.R. set on foot its admirable scheme of grants for research, the State had done nothing to help the graduate forward in his career. As is the case with the State scholarships, these grants are based on the financial circumstances of the applicants; reasonable certainty therefore exists that the provision of State aid is not abused by those who have the necessary means. How far it may be wise to hazard the suggestion I do not know, but the problem would be solved if, the first year's training (following immediately on graduation) being given in the graduating University (as was the case with the 1851 Exhibition Bursars and is permitted to the Carnegie Trust scholars), it were made a condition of renewal that the grantee migrate to another Institution. If further the renewal, in approved cases, could be extended to a third year and the maintenance grant increased during the one or two years' absence from home, I am convinced that the benefit to Chemistry, or to any other branch of science aided by the Department, would be not less pronounced than that associated with the 1851 Exhibition Scholarships.

Chemists no less than other scientific men are prone to be conservative in their outlook. It may be that the effect of any such change in research training might operate at first to the disadvantage of the smaller and less well equipped Universities—such a

possibility should, I venture to think, be accepted. It would at least furnish a criterion of relative efficiency which Governing Bodies could take to heart. In Germany before the War, entry into certain schools was more eagerly sought by research students than into others. If Germany could accept that position and did, why should we be reluctant to face it? If support be forthcoming for the view I have advocated, it is permissible to hope a way will be found to encourage the migration of students. How can it be otherwise when we remember that the outlook for the student of to-morrow and for Chemistry depends on the equipment of the student of to-day?

Openings in Industry for the Research Chemist.

I now turn to another point on which Professor Meldola touched in his Address—the existence of relatively few openings in chemical industry for the trained research chemist. Here, too, it is possible to recognise a change in outlook, despite the fact, which we all deplore, that acute depression in trade in 1920 and subsequent years led to a large amount of unemployment among industrial chemists and thus limited the opportunities of finding openings for postgraduates newly trained in research. Regrettable as this is, it can no longer be referred directly to apathy on the part of industrial firms, and for this reason. The D.S.I.R. was founded in 1916 not only to fulfil the valuable function of training University graduates in research but for the express purpose of stimulating industry by the foundation of research associations which by their example would in turn convince the respective industries of the supreme importance of research if trade is to be maintained in the face of intense, unresting competition.

These research associations, largely composed of manufacturers and in part financed by them, have in many cases had their original period of five years renewed, and incidentally have provided opportunities for research workers who presumably will be absorbed in the respective industries covered by the research associations. Moreover, it must be clear that for full advantage to be taken of the reports furnished by such associations, it is inevitable that an intelligence department manned by research workers must be installed in works which propose to utilise the information circulated to the industry concerned. In these respects, undoubtedly, the D.S.I.R. has laid industry under no less an obligation than academic work and done much to secure an outlet for the research worker trained in Universities and University Colleges.

But, repeatedly, the objection is urged by manufacturers that the University-trained product is of little use to them, is not

adaptable, cannot handle men, and becomes dissatisfied if the reforms which seem so obvious to him in the management of a works do not commend themselves forthwith to those in charge. And there is the innate idea in the minds of many that they should go into the research department or the control laboratories, rather than work their way up through the factory if called upon to do so.

If these faults exist, is it not at least possible that the University-trained man is not wholly to blame? What opportunity is afforded him of testing his vocation for industrial work? In the University, as at school or on the playing field, he has tested himself against his fellows under the only conditions known to him, and has formed some measure of his capacity to cope with the problems that arise in connexion with them. Transferred to a works, he needs time for readjustment to the new environment and during that period doubtless displays something less than the wisdom born of experience and age. The University trains the chemist and on the thoroughness with which that training has been applied to educate mind and eye and hand, its reputation as a chemical school depends. What does chemical industry do for the man who wishes to enter industry by way of the University? Does it afford him any opportunity of testing his vocation while there is yet time for him to make another choice? Does it help him in any way?

Before the War there was small opportunity for highly trained chemists to find their way into industry. Usually, the works trained their own chemical assistants who by the aid of evening classes and their own grit became efficient instruments for routine work. But that system is not likely to prove very helpful in the face of competition with America or Germany, where a better appreciation of the value of systematic training is found in the close relationship between University and factory. University and Industry—theory and practice—obviously must collaborate if the chemical industry of this country is to make headway in face of present difficulties.

Vacation Experience for Students in Chemical Works.

Early in 1917, the great corporation known as the Association of British Chemical Manufacturers came into being as the result, primarily, of action taken by the Council of this Society two years earlier in constituting itself a consultative body on all chemical matters arising out of the War. The history of the conferences and negotiations set on foot with the Councils of kindred societies and other bodies, which led to the formation of an industrial federation

unique in British chemical industry, has yet to be written. But our share in it emboldens me to ask whether it is not possible for some at least of the larger firms in the Association to allow selected students from Universities in their neighbourhoods to spend some part (say two months or ten weeks) of each Long Vacation in their works, not necessarily in laboratories but under foremen on the plant, working under factory conditions and thus becoming aware by actual experience of the kind of mental equipment required to deal with the problems that arise in connexion with large-scale working?

Two objections may be raised—the first that secret processes would no longer be protected and the second, that young students introduced into works in the way suggested would cause too much trouble, or their inexperience interfere too seriously with the routine. In reply, I can say that in Sheffield this problem has been faced and solved: it is the custom for intending graduates in Metallurgy to spend part of the Long Vacation in certain of the steel works in the City, to be welcomed there and to be placed under foremen to do such work as may be suggested. If this is possible, and there is this close association between the applied chemistry of the Metallurgical school and the steel works, in which secret processes if they exist anywhere would be likely to be found, is it too much to hope that something of the same kind may be introduced into chemical works for the good of all concerned? The works would be able to pick their men in course of training and, doubtless, the University studies of such picked men after graduation could be directed to the type of work which would be of use later on.

I am fully aware that industrialists, managing directors among them, assert in no uncertain tones that the Universities do not know how to train men to be of use to them. To my mind the criticism is just as helpful or the reverse as that pronounced by University professors who assert with equal confidence that the works, through lack of scientific control, are courting the fate which in their view deservedly awaits them. Such pronouncements carry us nowhere: what is beyond measure needed is some scheme of co-operation with a real intention and endeavour to devise a means by which the University may become more helpful to the manufacturer and the manufacturer to the University. United, I feel sure we can face the world—divided and unhelpful the one to the other, we shall have done nothing, despite the lessons of the War, to improve upon the state of things to which Professor Meldola made such regretful allusion.

Community of Interests among Chemists.

I have assumed that this Society represents more the University or academic side of chemistry and the A.B.C.M. the industrial side. Between them is found that vigorous body of industrial chemists, the Society of Chemical Industry, and its President, Mr. Woolcock, is, as we know, the Manager of the A.B.C.M. He will forgive me if I suggest that the moment is propitious for an advance to be made and that during his Presidency he will render chemistry a lasting service if he can take the first steps towards promoting a closer working between the two sides—a better appreciation of one another's difficulties and a sincere attempt to resolve them. The Pure Chemistry exhibit in the Wembley Palace of Industry owed much to his genius for overcoming difficulties. I allude to it not merely as showing that pure chemistry, like applied chemistry, can enter into association for the common good, but rather to draw attention to the fact that the Pure Chemistry exhibit was separated by a partition from its applications in industry—chemistry pure and applied being separated by a screen. True there were openings from the one side to the other, but they were small in comparison with the area covered by the screen—and to my mind that screen symbolised "the middle wall of partition" between the two sides of chemistry, which perhaps no one person could take more effective steps to break down than my brother President, who by singular good fortune happens to be a member of the three bodies concerned.

In its approach to the Society of Chemical Industry, leading up to the foundation of the Bureau of Abstracts and to co-operation in other directions, this Society has shown itself willing to go some part of the way towards a closer community of interest—the future alone can show whether these and other like efforts will have their fruition in the development of a corporate union of chemical interests, which shall ensure for chemistry the recognition which is its due in the national estimate of the importance of science in promoting the welfare and progress of the Empire.

I cannot sit down without expressing my sincere thanks to the Officers, Council and Fellows of the Society for the kindness shown by them during my period of office; to Mr. Carr, Mr. Clifford and the house staff for assistance rendered readily and willingly at all times, for which I cannot find words wherewith adequately to convey my appreciation; and to the members of my staff at Sheffield who have made it possible for me to maintain the tradition that the President should be in the Chair at all meetings of the Society. That the same kindly feeling may be extended to my successor is a request which I am sure is granted even before it is

made—he brings to the office much experience gained on the one hand in the conduct of its affairs as Honorary Secretary and Foreign Secretary, and on the other in academic life, in the Army, and now as Director of one of those important research associations to which reference has been made. In view of such a record, we may indeed feel sure that the great traditions of this Society will be safe in his hands.

OBITUARY NOTICES.

GEORGE THOMAS BEILBY.

BORN NOVEMBER 17TH, 1850: DIED AUGUST 1ST, 1924.

GEORGE THOMAS BEILBY was born in Edinburgh, where his father was in practice as a physician, and was educated at private schools and at the University of his native city. In 1877 he married Emma, daughter of the Rev. S. Newnam, by whom he is survived, as also by a son, Hubert N. Beilby, who is technical director of the Cassel Cyanide Company, and a daughter, the wife of Professor Soddy.

In 1869, at the age of nineteen, Beilby entered upon an industrial career of remarkable success by accepting a post as chemist with the Oakbank Oil Company, and very soon after his appointment proceeded to give proof of the originality and skill as an investigator which he continued to manifest during the whole of his working life. He attacked the problem of the distribution of the nitrogen in bituminous shale when it is distilled for the production of paraffin oil, and a long series of laboratory and large-scale experiments, carried out largely by himself and partly in collaboration with William Young, resulted in the introduction of improvements in plant and in methods of manufacture which gave a new lease of life to the paraffin oil industry in Scotland. A brief account of this work is contained in an important paper "On the Production of Ammonia from the Nitrogen of Minerals," which he contributed to the Glasgow Section of the Society of Chemical Industry in 1884, and was the first of a large number of memoirs on scientific and technical subjects communicated to the Royal Society, the Chemical Society, the Society of Chemical Industry, the *Philosophical Magazine*, the *Reports* of the British Association, etc.

For a number of years Beilby carried on invaluable work in this field of industry, but after the introduction of the cyanide process for the extraction of gold he directed his attention to the discovery of new methods for the production of alkali cyanides. In 1891 he patented a process which was set in operation, under his care, by the Cassel Cyanide Company and developed into a large and successful industry.

Certain observations made in connexion with his cyanide process led Beilby to enter upon the series of brilliant investigations into the physical properties and especially the microstructure of metals and other solids in different states of aggregation, which he continued

to prosecute until near the end of his life. The results of these investigations, many of which had an important bearing on metallurgical problems, are summed up in a masterly volume on "The Aggregation and Flow of Solids" which he published in 1921.

From the very beginning of his industrial career Beilby took the keenest interest in the question of fuel economy. He made a special study of this subject, and in 1903 presented an exhaustive report to the Royal Commission on Coal Supplies, in which he emphasised the enormous waste of coal in this country, with the attendant production of smoke and dirt in our large cities, through inefficient combustion. In 1912—1913 he served on Lord Fisher's Committee on Fuel and Engines for the Navy, and the conclusions arrived at by that Committee were largely based on the great amount of pioneering experimental work on low-temperature carbonisation which had been carried out under his direction in the works of the Cassel Cyanide Company. The importance of this subject led to the establishment, in 1917, of the Fuel Research Board by the Department of Scientific and Industrial Research, and Beilby, who was already a member of the Advisory Council, was appointed Chairman and Director of Research. He held this post until he found it necessary to retire in 1923, and the value of his services is attested by the following tribute paid to him by the Committee of the Privy Council for Scientific and Industrial Research:

> "to him the creation of the necessary organisation and the design and building of H.M. Fuel Research Station at East Greenwich are solely due. He, more than any other man, put the scientific knowledge of low-temperature carbonisation on a firm basis; his work on gas standards had a formative influence on recent legislation for the gas industry, and his skill as a microscopist opened up a fascinating direction for research into the structure and behaviour of coke. It is with the deepest regret that we lose his wise and experienced counsel and the great scientific and practical knowledge he brought to the many difficult questions with which the Department in the early years of its existence had to deal. We desire on behalf of the Government and the nation to place on record our high appreciation of all that he so generously and freely gave them both during the War and in the hard and critical years which have succeeded it. Through all, his aim and effort were to help to the utmost the re-establishment of this land and people."

It should be added that during the War Beilby took an unremitting and highly esteemed part in the activities of the Trench Warfare Committee and the Naval Board of Invention and Research.

Beilby also took a deep and active interest in educational matters. In 1907 he was elected Chairman of the Governors of the Royal Technical College, Glasgow, and remained in office for sixteen years. His scientific attainments, his capacity for organisation, and his enlightened generosity were of the utmost importance to the College during the most active period of its development, and his sympathy with the members of the staff in their efforts to augment the opportunities for the prosecution of research work in each department took a very practical form. He was a strong advocate of technical education and always emphasised the necessity of securing the co-operation of the leaders of industry in modelling technical institutions. Impressed as he was with the importance of the fuel question, soon after his appointment as Chairman he arranged for the equipment of special laboratories in the College for instruction and research in fuels, these being the first of their kind in this country.

Beilby's eminent services to the State, to science, to industry and to education did not pass without recognition. He received the honour of knighthood in 1916. He was elected to the Royal Society in 1906 and was a member of the Council from 1917 to 1919 and a Vice-President in 1919. He also served as President of the Society of Chemical Industry (1898—1899), of the Institute of Chemistry (1909—1912), of the Institute of Metals (1916—1918), and of the Chemical Section of the British Association on the occasion of the meeting in South Africa in 1905. He received the Honorary Degrees of LL.D. from the Universities of Glasgow and Birmingham, and D.Sc. from the University of Durham.

Sir George Beilby was not only a leader of industry but above all a very zealous student of science from his early days in the University until failing health compelled his withdrawal from most of his activities, and his career bears eloquent testimony to the importance of scientific research to industry. One of the most modest and unassuming of men, his wide knowledge, well-balanced judgment, clearness of thought, and charm of manner made a deep impression upon all who came in contact with him in public and in private life. His integrity and directness rendered him impatient with anything that savoured of sham or pretence, but an earnest worker was always assured of his sympathy and encouragement. His generosity was inexhaustible, but, characteristically, was kept hidden except from very few. To all who worked with him his example will be an abiding inspiration.

G. G. H.

HENRY GEORGE SMITH.

BORN JULY 26TH, 1852; DIED SEPTEMBER 19TH, 1924.

HENRY GEORGE SMITH was born in 1852 at Littlebourne, in Kent, and he was educated at the neighbouring schools of Ickham and Wingham, and subsequently under the private tuition of the Rev. Mr. Midgley, M.A. Although possessing a decided bent for science, prior to his arrival in Australia for health reasons, in 1883, circumstances had prevented him from pursuing scientific studies. In the following year, however, he availed himself of an opportunity of joining the staff of the Sydney Technological Museum, then housed in the Domain, in a semi-scientific capacity. The next few years were utilised to the full by Smith in increasing his knowledge of science, particularly of chemistry; his efforts in this direction were warmly encouraged by the late Mr. W. A. Dixon, F.I.C., who was at the time lecturer in chemistry at the Sydney Technical College. Smith maintained a great interest in this institution, and from 1898 to 1911 he lectured to the evening classes at the College in organic chemistry.

In 1891, Smith was appointed laboratory assistant at the Technological Museum. The same year witnessed the publication of his first original paper, which appeared in the *Proceedings* of the Linnean Society of New South Wales, and announced the discovery of barytes in the Hawkesbury sandstones at Sydney. It is noteworthy that Smith was then thirty-nine years old. In 1895, he was appointed to the position of mineralogist at the Museum. By this time he had published five original papers, dealing with inorganic chemistry. In the same year appeared his first contribution to organic chemistry: a paper on eucalyptus kinos and the occurrence of eudesmin, published in collaboration with Mr. J. H. Maiden, in the *Proceedings* of the Royal Society of New South Wales. This paper was destined to assume peculiar significance, as the precursor of a long series of original publications dealing with the chemistry of the Australian flora. Smith's first original contribution to the chemistry of the Australian essential oils was carried out in collaboration with Mr. R. T. Baker, F.L.S. (late Curator and Economic Botanist of the Sydney Technological Museum), in 1897, the species concerned being the Sydney Peppermint (*Eucalyptus piperita*). The oil of this particular species had been distilled as far back as 1788 and used as a substitute for ordinary peppermint oil by Dr. White, Surgeon-General to the first settlement. In 1900, Smith was successful in isolating the substance giving rise to the characteristic odour; he showed it to be a ketone, $C_{10}H_{16}O$, and named it piperi-

tone. Many years later (J., 1924, **125**, 129) this ketone, the lævorotatory form of which has a wide distribution in the genus *Eucalyptus*, was shown to be chemically identical with Δ^1-*p*-menthen-3-one, synthesised by Wallach in 1908. Curiously, the dextrorotatory modification of this sole ketonic constituent of eucalyptus oils was identified in the essential oil of a Himalayan grass, *Andropogon Jwarancusa*, by Simonsen, during the progress of the later investigations of Smith and his collaborators (J., 1921, **119**, 1644).

In 1899, Smith was appointed Assistant Curator and Economic Chemist at the Museum, and his tenure of this post lasted until his retirement from the Government service in 1921; altogether he was associated with the Sydney Technological Museum for thirty-seven years. Most prominent among his record of accomplishment during this period stands the extensive series of researches into the chemical nature of the essential oils of the genus *Eucalyptus*. This work, which was conducted throughout in close collaboration with his botanical colleague, R. T. Baker, resulted in the establishment of a remarkable correlation between chemical and botanical characteristics in this complex genus, which includes some 250 distinct species. The examination of the essential oils of a numerous selection of species, representative of the Australian mainland and of Tasmania, revealed the presence of more than 40 distinct components; moreover, the oil from any particular species was found to show a remarkable constancy of composition; and each chemical constituent appeared to increase in amount through a certain range of species until it reached a maximum. A connexion was also traced between certain morphological characters, such as the type of the leaf venation, and the chemical nature of the corresponding oil: thus, a "feather" venation indicated the presence of pinene and possibly bornyl acetate; an intermediate venation was associated with the occurrence of pinene and cineole; and a "butterfly-wing" venation denoted phellandrene, and possibly piperitone or geranyl acetate.

A main outcome of these phyto-chemical researches, which included the detailed examination, not only of the essential oils, but also of the astringent exudations of more than 100 eucalyptus species, was the advancement by Baker and Smith of an evolutionary theory dealing with the chronological sequence in this genus and the older and related genus *Angophora*. The preliminary work, extending over a period of six years, was published in 1902, in a volume entitled "A Research on the Eucalypts, especially in regard to their Essential Oils." A revised edition of this *magnum opus* of Australian science, containing the results of a further eighteen years' observations, was published in 1920. The trend of

other investigations carried out by Smith, again largely in collaboration with Baker, indicated that this fruitful idea of chemical and botanical correlation is also destined to lead to valuable results in other typical Australian genera. The work summarised in "A Research on the Pines of Australia" (Sydney, 1910) may be referred to as an example, and further investigations were directed towards the melaleucas, leptospermums, boronias, and other widely distributed groups. The two volumes on the Eucalypts and the Pines of Australia are regarded as authoritative.

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From about 1914 onwards, Smith became informally but actively associated with the newly-founded Department of Organic Chemistry at the University of Sydney, and upon his retirement from the Technological Museum in 1920 he continued to work assiduously at the University upon the chemical constitution and reactions of piperitone, α-phellandrene, and other components of Australian plant products, which had figured in his earlier work. The accounts of these later investigations were published in the Chemical Society's *Journal* (J., 1924, 125, 129, 930; etc.); but the fact that his sense of local patriotism and his modesty induced him to publish the bulk of his work in Australia, rather than in Europe, undoubtedly prevented his researches from attracting in full measure the general attention which they so richly merited. Altogether, Smith published well over 100 original contributions to chemical science, and of these, 62 appeared in the *Proceedings* of the Royal Society of New South Wales. The occasion of his retirement from the Sydney Technological Museum, in 1921, in the general opinion of Australasian workers in science, offered a fitting opportunity for the award to him of some higher form of recognition than he had hitherto obtained for his eminent services to Australian science and Australian economic development. It is pleasing to record that in the following year he received the David Syme Prize of the University of Melbourne, which is given for original scientific research connected

with the material and industrial development of Australia. The high esteem in which Smith was held among Australasian men of science is evidenced by his election to such offices as the Presidentships of the Royal Society of New South Wales (1913), the New South Wales branch of the Australian Chemical Institute (1922—1923), and the chemistry section of the Australasian Association for the Advancement of Science. In the last-named capacity he delivered his presidential address on the chemistry of the Australian flora at Wellington, New Zealand, in 1923. He was also an original member of the Australian National Research Council, and he conducted a good deal of valuable work under the auspices of the Commonwealth Institute of Science and Industry.

Smith died at Roseville, Sydney, on September 19th, 1924, at the age of seventy-two. He was twice married, and left a widow and family, including three sons. In all the relations of life quietly genial and considerate, Smith was distinguished by his modesty and sincerity. One of the most selfless of men, he achieved without seeking it a world-wide reputation; but his reward lay in his work and in his sure knowledge of the part it was destined to play in the economic development of his adopted and beloved land of Australia. Even after passing the three score years and ten, his natural ardour and activity for chemical investigation remained in full measure. To those of the younger generation of Australian chemists who were so fortunate as to be associated with him, his unfailing enthusiasm will act as a lasting inspiration. His practical knowledge of Australian natural products was profound. In the laboratory, his diagnosis of the chemical composition of an essential oil after a few rapid superficial tests was a revelation; in the bush, the tall trees were to him as familiar friends, and his intimate knowledge of their characteristics seemed at times to border upon wizardry. In spite of initial disabilities, including lack of preliminary training, and more lasting handicaps, such as complete isolation from any centre of organic chemical activity, and with less than could have been desired in the way of encouragement and material recompense, Smith devoted well over thirty years of incessant research to the elucidation of the chemical and economic significance of these products. To the last, he was an ardent, tireless worker, who regarded every hour in the spirit of the true man of science as a potential "bringer of new things"; to the last, he remained strong in will to bring the secrets of Nature into the service of man. His pioneering work is not only of high scientific and economic worth: it will remain to him a unique and enduring monument in the annals of Australian science.

JOHN READ.

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